4257

Final Technical Report | *October 1962 to December 1963*

SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950324
UNDER NASA7-100

JPL COGNIZANT ENGINEER: ROBERT HARRINGTON

STANFORD RESEARCH INSTITUTE

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SRI Project Supervisor: R. F. Muraca

SRI Project No. PLU-4257

Approved:

R. F. Muraca

R. F. MURACA, ASSISTANT GENERAL MANAGER
PHYSICAL SCIENCES RESEARCH

Copy No. 171

FOREWORD

This final report summarizes the work accomplished by Stanford Research Institute during the period October 1962 to December 1963 under Contract No. 950324 for the Jet Propulsion Laboratory of the California Institute of Technology.

Mr. Robert Harrington of the Jet Propulsion Laboratory's Materials and Methods Group was Cognizant Engineer for the project.

The technical effort at Stanford Research Institute was directed by Dr. R. F. Muraca, Assistant General Manager of the Physical Sciences Research Area.

As requested by the Cognizant Engineer, the Institute staff members responsible for the various phases of the project are identified in the appropriate Sections of the report.

ABSTRACT

Stanford Research Institute, Menlo Park, California
SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS
Final Technical Report, October 1962 to December 1963
R. F. Muraca et al., December 8, 1963, p.
(NASA Contract NAS7-100; JPL Contract 950324; SRI Project PLU-4257).

The thermal degradation of a group of "space grade" polymers in vacuum was studied; degradation of the skeletal structure at temperatures below 125°C was not observable. Several mechanisms for the degradation of polyurethane polymers at temperatures in excess of 150°C are proposed. The syntheses of various deuterated nylons and nylon precursors are described; these materials are for future studies of the mechanism of degradation.

An apparatus and procedure for determining volatile condensable material given off by polymers at 125°C are described; it is shown that the procedure is of use only for determining the extent to which warm polymers release material which can condense on cooler surfaces and polymerize. It is recommended that mass spectrometric studies of volatile materials be used to determine the quality of "space grade" polymers.

Apparatus and procedures for determining physical properties in a vacuum-thermal environment are described; data obtained thus far permit no conclusions to be drawn.

Polymers studied include Vitons, Mylars, silicone rubbers, Teflons, polyurethanes, and nylons.

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I. INTRODUCTION AND SUMMARY

This Final Report summarizes the work done under JPL Contract No. 950324, SRI Project No. PLU-4257, during the period October 1, 1962 to November 30, 1963. Interim Report No. 1, June 8, 1963, described in detail the design of equipment constructed for the various studies, summarized the techniques of operation, and discussed some preliminary results.

The broad objective of the program of work is to provide a definitive study of the effect of high vacuum and elevated temperature on certain classes of the polymeric materials which are known to be suitable for use in spacecrafts. The work undertaken thus far in this long-range program was designed: (1) to ascertain the extent to which warm polymers release substances in a vacuum which condense at temperatures in the vicinity of 25°C; (2) to determine if polymers undergo gross skeletal degradation in a vacuum at temperatures in the vicinity of 125°C; (3) to determine, if possible, mechanisms by which polyurethane and nylon polymers might be degraded in space environment; (4) to determine changes in pertinent physical properties of selected polymers in a thermal-vacuum environment. The commercial polymers selected for study are: Vitons A and B, GE silicone rubbers SE-555 (standard, + Fe_2O_3, + TiO_2), Teflon TFE and FEP, Mylars, and nylon.

The work performed during this phase of the long-range program permits the following conclusions at this time:

(1) The apparatus and procedure for determining volatile condensable material are satisfactory; however, it was ascertained that the only value of the V. C. M. determination is for those polymers which release polymerizable material. It was shown that "space grade" polymers do not release polymerizable material and that mass spectrometric studies of volatiles are to be preferred.

(2) Mass spectrometric studies of material released by "space grade" polymers at temperatures of the order of 125°C and vacuum better than 10^{-7} mm of Hg indicated no observable degradation of the skeletal structure of the polymers. The majority of components released by polymers are identifiable by mass spectrometry.

(3) Some inroads were made in the determination of mechanisms by which polyurethane polymers are degraded by heat in a vacuum; the mechanism of degradation in a vacuum at temperatures in excess of 150°C is significantly different for some polyurethanes than it is in air. Mass spectrometric studies of the polyurethanes at temperatures below 125°C disclosed no degradation products; therefore, the degradation mechanisms occurring in polyurethanes at higher temperatures are undetectable at the moderate temperatures expected in spacecrafts.

Considerable work was expended in synthesizing deuterated nylons preparatory to study of their thermal degradation; these compounds are available for future study.

(4) Data available at this time from the work performed during this phase of the program do not permit drawing conclusions as to the effect of the thermal-vacuum environment on the physical properties of polymers.

II. VOLATILE CONDENSABLE MATERIAL

R. F. Muraca

The objective of this part of the program of study was to determine the extent to which volatile material, released from polymeric substances in vacuo at a temperature of 125°C, will condense on a surface maintained at about 25°C.

The apparatus for the determination of volatile condensable material (V. C. M.) was designed and constructed during the first six months of this program; since that time, only minor modifications have been made. Complete design drawings and photographs are presented in Interim Report No. 1, Figures III-1 to III-9. The over-all schematic of the V. C. M. unit cluster and an illustrative photograph are included in this report as Figures II-1 and II-2, respectively. Minor changes made in the apparatus can be determined by comparison of Figure II-1 in this report with Figure III-1 of Interim Report No. 1.

The method of performing the V. C. M. determination is quite straightforward: Samples of about 3 g are weighed on a microbalance to ± 0.005 mgm, and then wrapped around the heaters shown in Figure II-1. Then the clean, polished copper plugs (also indicated in Figure II-1) are weighed on the microbalance (about 21 g). When the V. C. M. apparatus is completely assembled and set in place in the vacuum chamber, the system is exhausted at room temperature to a pressure of about 5×10^{-6} mm of Hg (cold traps). Then the individual heaters are turned on and cryopumping is initiated. After a prescribed period, the run is terminated and the system is vented with helium. The polymeric samples and the copper plugs are then re-weighed on the microbalance.

Two sets of duplicate samples occupy four of the six V. C. M. units shown in Figure II-1; the other two V. C. M. units, with weighed copper plugs, are run as controls.

Vitons (vinylidene fluoride-hexafluoropropylene)

Duplicate samples of about 2.8 g each of Viton A and Viton B were maintained in the V. C. M. apparatus for a period of two weeks. The weight of condensed material (on the 1"-diam copper plugs) and the weight-loss of the samples are reported in Table II-1. Viton B, allegedly more thermally-stable than Viton A, suffered a weight-loss of only 0.13% compared to 0.43% for Viton A, and a V. C. M. weight of 0.25 mgm compared to 0.52 mgm for Viton A. It is interesting to note that the mass spectrometer study (see Section III) indicates less production of volatile material for Viton B than Viton A, and also a lesser weight loss for Viton B.

Silicone Rubbers

A preliminary 30-hr run on G.E. silicone rubber SE-555 + Fe_2O_3 resulted in an average V. C. M. of about 0.4 mgm; an oily substance was deposited on the copper plug and there was no condensed matter on the control plug. Runs made with G.E. silicone rubber SE-555, standard, had poor replication and repeated tests were confusingly similar in performance.

A series of additional experiments were performed, and their outcome led to the following reflections:

The Langmuir equation permits estimation of the rate of evaporation of a pure compound:

$$W = \frac{P}{17.14}\sqrt{\frac{M}{T}}$$

where W = rate of evaporation in $gm/cm^2/sec$

M = molecular weight

T = absolute temperature

P = vapor pressure in mm.

The vapor pressure of pure compounds may be expressed by the equation:

$$\log P_{mm} = A - \frac{B}{T}$$

and this is easily transformed to

$$P_{mm} = 10^{A - \frac{B}{T}}$$

Now, if it is desired to compare the rate of evaporation of a compound at two temperatures, it is obvious that the Langmuir equation can be combined with the exponential form of the vapor pressure expression to yield:

$$\frac{W_1}{W_2} = \frac{10^{A - B/T_1}}{10^{A - B/T_2}} \sqrt{\frac{T_2}{T_1}}$$

where the subscript 2 refers conveniently to the higher temperature.

Thus, in the instances of the V. C. M. determination, where the higher temperature is 125°C (398°K), the rates of evaporation at the two temperatures are related by the equation:

$$\frac{W_{398}}{W_{298}} = 0.8653 \left(\frac{10^{A - B/398}}{10^{A - B/298}} \right)$$

As an indication of the vapor pressures expected from silicone polymers, the work of Wilcox [1] was consulted; data given in this reference include the vapor pressure equations for compounds of the general form:

$$(CH_3)_3SiO_{1/2}\left[(CH_3)_2SiO\right]_x (CH_3)_3SiO_{1/2}$$

The coefficients A and B of the vapor pressure equations given in the reference are plotted in Figure II-3 and extrapolated to lower molecular weight values purely for sake of example. Using the data of Figure II-3, the ratios of evaporation rates for various molecular weight compounds were computed; these are

[1] Wilcox, D. F., J. Am. Chem. Soc., 68, 691 (1946).

summarized below:

RATIO OF EVAPORATION RATES AT 398°K AND 298°K

No. of Si Atoms	M. W.	W_{298}	Ratio $\frac{398°K}{298°K}$	Ratio $\frac{373°K}{298°K}$
18	1346	1.5×10^{-9}	578,000	32,400
12	902	3.6×10^{-4}	28,000	3,600
6	458	1.62	430	129

The ratios obviously indicate that the silicone materials evaporate much faster at 398°K than at 373°K (578,000 to 32,400); more importantly, however, the higher molecular weight material is evaporated at an enormous rate at higher temperatures than at lower temperatures, but the rate of evaporation of the lower molecular weight material is (relatively) not influenced very much by an increase in temperature, and the lower molecular weight material evaporates millions of times faster than high molecular weight material at temperatures between 298 and 398°K.

Now, in the case of a polymeric material consisting of a distribution of various molecular weights, it is difficult to make quantitative predictions of evaporation rates at various temperatures; the rates are nearly impossible to compute when various effects such as diffusion of species through a molecular matrix, nonideal vapor pressures, and impermeable surface layers are involved. Nevertheless, qualitative generalizations may be drawn about the results of a V. C. M. determination provided impermeable membranes are not formed and the resin sample is thin enough (or porous) so that diffusion effects are negligible. Referring to Figure II-4, the upper (solid-line) curve in the upper graph indicates the cumulative loss of weight in a vacuum expected from a resin (say at 398°K) which has volatile matter consisting of a more or less uniform distribution of molecular weight species. The solid-line curve in the lower graph represents the cumulative loss from a resin which has a preponderance of low molecular weight species in the volatile matter. The dotted-line curve in each graph represents, qualitatively, the cumulative weight on a cold (298°K) collector which receives (straight-line) the material released by the warm resin in a V. C. M. apparatus; an attempt is made, in these graphs, to show

that the material collected on the cold collector evaporates slowly and that the weight of material on the cold collector is never stable.

The interesting point not brought out by the graphs in Figure II-3 is that the weight of material on the collector plate after a very long time continues to rise slowly if the resin continues to give off high molecular weight substances, but that the weight on the plate will eventually be zero if the resin ceases to give off material early in the test. Additionally, the graphs do not give any idea of the times involved, but it is important to realize that the relative evaporation rate data tabulated above indicate that enormous times at 298°K are required to remove thin films of high molecular weight material; for example, for an 18-atom silicone, the weight of material evaporated in one hour at the higher temperature (398°K) will require 578,000 hours for evaporation at 298°K! Moreover, since the evaporation rates of high molecular weight materials are small, an exceptionally long time is required to remove volatile material of this type from resins, and, as indicated in the graphs of Figure II-3, a very long time must be utilized in the determination of V. C. M. to obtain weights of material on the cold collector plates which have "leveled off."

As was mentioned earlier in this section, a series of experiments were performed with G. E. silicone rubbers SE-555 standard (grey in color) and SE-555 + TiO_2 (white in color); the series of experiments involved determination of V. C. M. collected after 72 hours, 168 hours, and 336 hours. The data obtained from these experiments were plotted in Figure II-5 and curves were drawn through the appropriate points. In so far as V. C. M. data are concerned, the plots in Figure II-5 might be considered as the portions of the graphs in Figure II-4 which are marked "A," and one is led to the conclusion that the grey silicone rubber (SE-555 standard) has a preponderance of easily volatile material and thus corresponds to the lower of the graphs of Figure II-4; additionally, since at 336 hours the amount of residual material on the cold plate of the grey rubber is more than on the plate of the white rubber (and this is decreasing), it may be assumed that the grey rubber has a higher content of high molecular weight distillate.

Of course, one can take the stand that the entire discussion of V. C. M. given above and the graphs of Figure II-4 are purely conjectures tempered to

some extent by available theoretical treatments (like the Langmuir equation) and, indeed, such a stand is in order. For example, one could have assumed other distributions of the various molecular species in a resin and have obtained a set of curves for the cumulative weights on cold plates which would have resembled the data plots of Figure II-4; the conclusions then would be probably different than the ones drawn above. However, a detailed examination of Table III-6 summarizing the mass spectrometer studies of the materials given off by the silicone rubbers under discussion clearly show that the conclusions drawn above from the V. C. M. data are completely valid in this instance.

It appears, therefore, that some success can be had in interpreting the state of affairs in a resin from V. C. M. data, especially if curves such as shown in Figure II-5 can be obtained; however, no assurance of the validity of interpretation is possible without auxiliary data from more diagnostic procedures such as are offered by mass spectrometry.

Conclusions

The following conclusions may be made based on the work performed thus far:

(1) The determination of the cumulative volatile condensable material (V. C. M.) for periods of time between 75 and 400 hours gives an indication of the molecular weight distribution in the material volatilized from a resin.

(2) Times of the order of 1000 hours and longer are required to obtain a true measure of V. C. M.

(3) The V. C. M. procedure is valuable for determining the degree to which condensed material polymerizes and becomes nonvolatile, and the procedure should be used exclusively for this purpose.

(4) The mass spectrometer is a better and more rapid indicator of the nature and qualities of the material volatilized from a resin than the V. C. M. method (but not for polymerizability of the residues).

(5) Rigid control of temperatures and vacuum conditions are necessary in V. C. M. procedures; simple heating apparatus and vacuum systems will give values for V. C. M. that are not indicative of the behavior of resins in a space environment.

Recommendations

The procedure developed and the apparatus constructed for the determination of V. C. M. is satisfactory and gives reasonably reproducible values. The V. C. M. determined as a function of time is particularly significant and may be used for "space grade" polymers to screen the effects of pretreatments, etc. However, most of this information can be obtained simply and relatively rapidly with a mass spectrometer and with a greater degree of assurance. Thus, it is recommended that the V. C. M. procedure be abandoned for routine work and be used only when it is desired to determine the extent to which volatile materials polymerize on condensation. In these instances, the time for the determination must be prolonged to more than 1000 hours and auxiliary information must be obtained by mass spectrometry.

TABLE II-1

SUMMARY OF V. C. M.* DETERMINATIONS ON VITONS

Polymer	Weight of V. C. M.	Weight Loss of Polymer
Viton A, DuPont	0.52 mgm ± 0.12	0.43% ± 0.04
Viton B, DuPont	0.28 mgm ± 0.04	0.13% ± 0.02

*V. C. M. = Volatile Condensable Material
Time, 336 hrs; Pressure, 1×10^{-6} mm of Hg
T_{sample}, 125°C; $T_{condensing\ surface}$, ~25°C

TABLE II-2

SUMMARY OF V. C. M.* DETERMINATIONS ON SILICONE RUBBERS

Time	Weight of V. C. M.		Weight Loss of Sample	
	SE-555 standard	SE-555 + TiO_2	SE-555 standard	SE-555 + TiO_2
72 hrs	0.58 mgm ± 0.009	0.33 mgm ± 0.003	0.24% ± 0.05	0.16% ± 0.02
168 hrs	0.32 mgm ± 0.004	0.28 mgm ± 0.004	0.33% ± 0.03	0.16% ± 0.00
336 hrs	0.34 mgm ± 0.030	0.13 mgm ± 0.010	3.14% ± 1.6**	0.13% ± 0.04

*V. C. M. = Volatile Condensable Material

Pressure, 1×10^{-6} mm of Hg; T_{sample}, 125°C; $T_{condensing\ surface}$, ~ 25°C

** Precision is obviously poor and the results are reported merely for the record; an independent determination (see Table III-6) indicates a value of 0.78%.

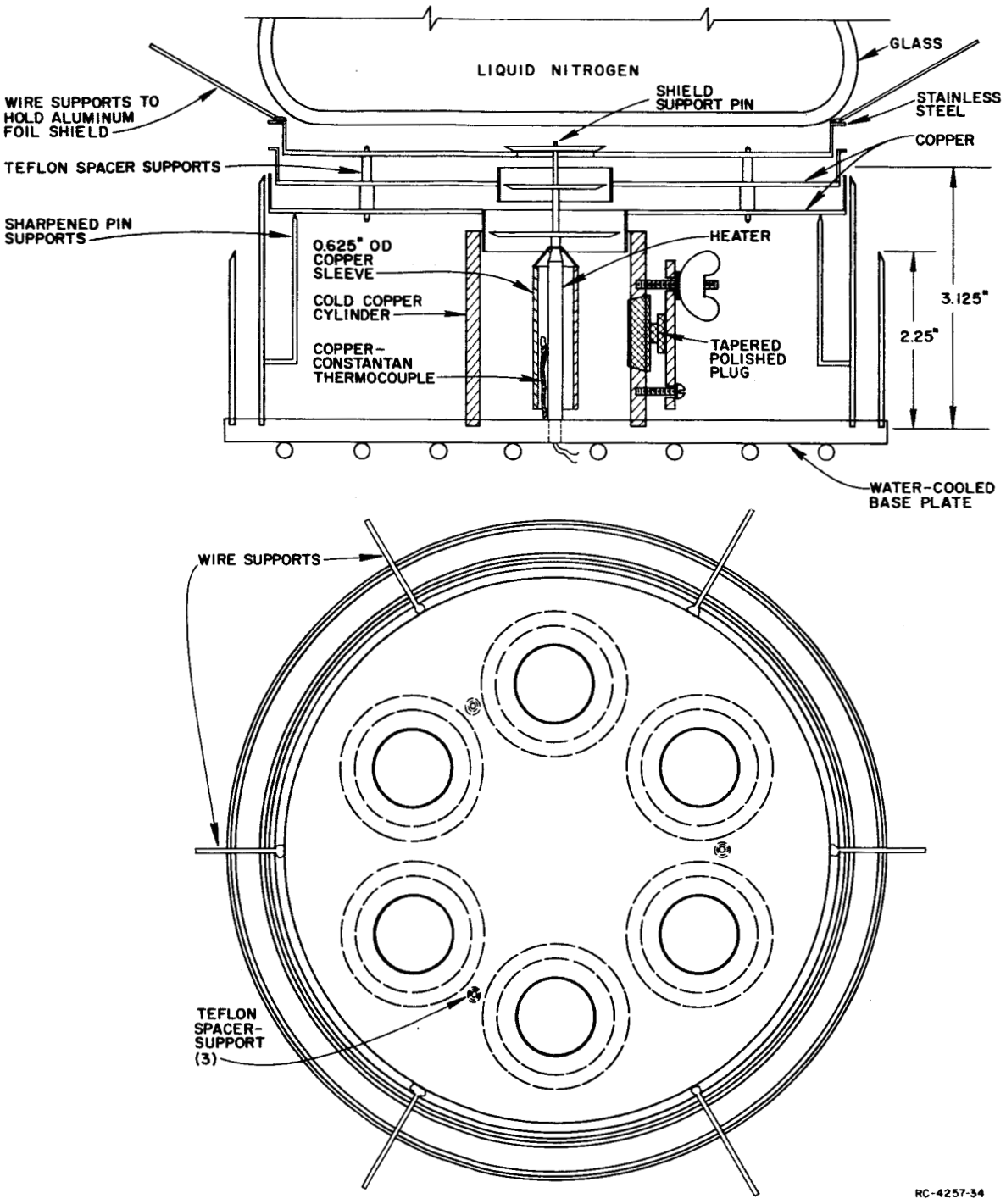


FIG. II-1 SCHEMATIC DIAGRAM OF A SINGLE V.C.M. UNIT AND ARRANGEMENT OF A CLUSTER OF SIX UNITS

FIG. II-2 INTERNAL VIEW OF VCM APPARATUS SHOWING ARRANGEMENT OF HEATER-COLLECTOR ASSEMBLIES AND SHIELDS

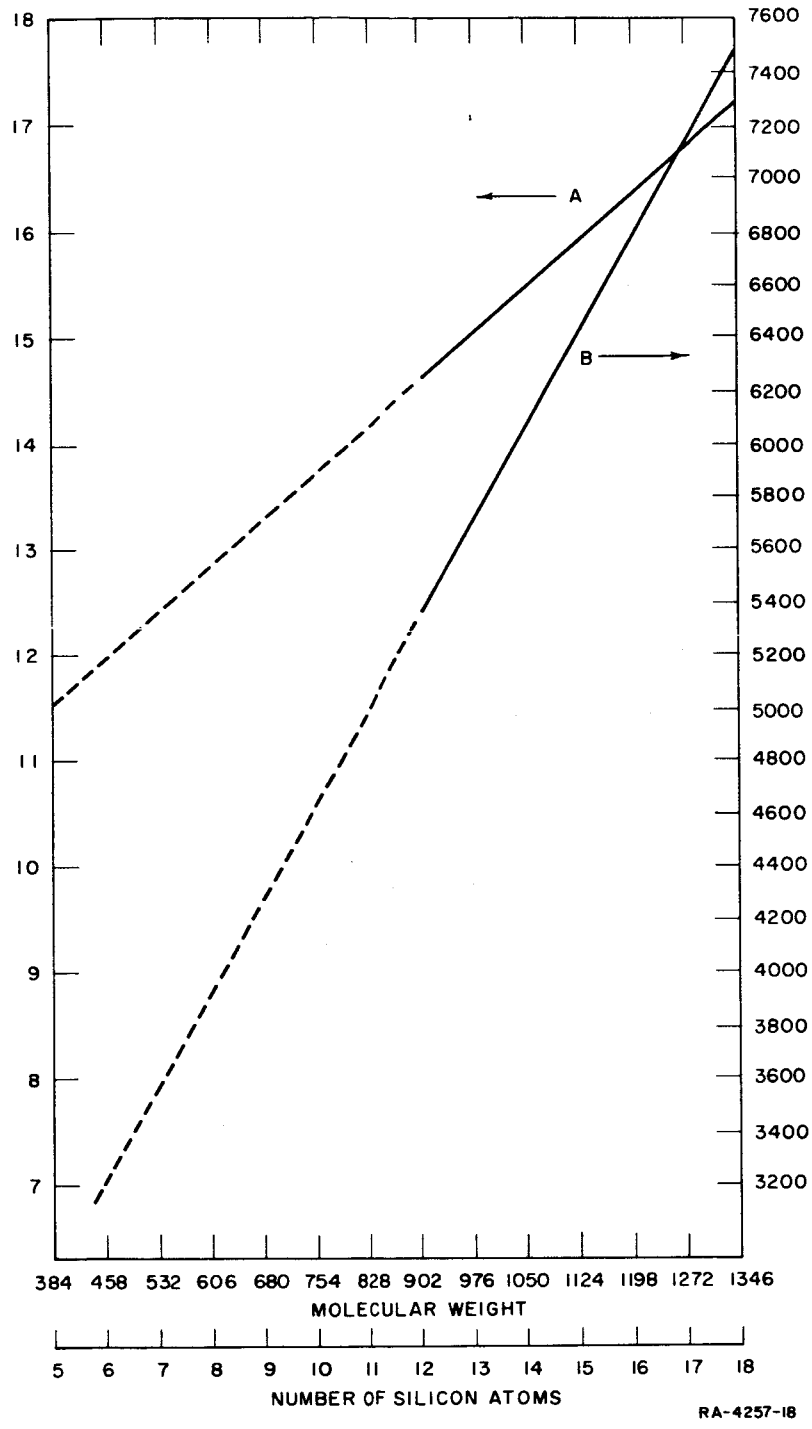


FIG. II-3 COEFFICIENTS IN THE VAPOR PRESSURE EQUATION
$\log P = A - B/T$ FOR COMPOUNDS OF THE GENERAL FORMULA:

$$(CH_3)_3SiO_{1/2}\left[(CH_3)_2SiO\right]_x(CH_3)_3SiO_{1/2}$$

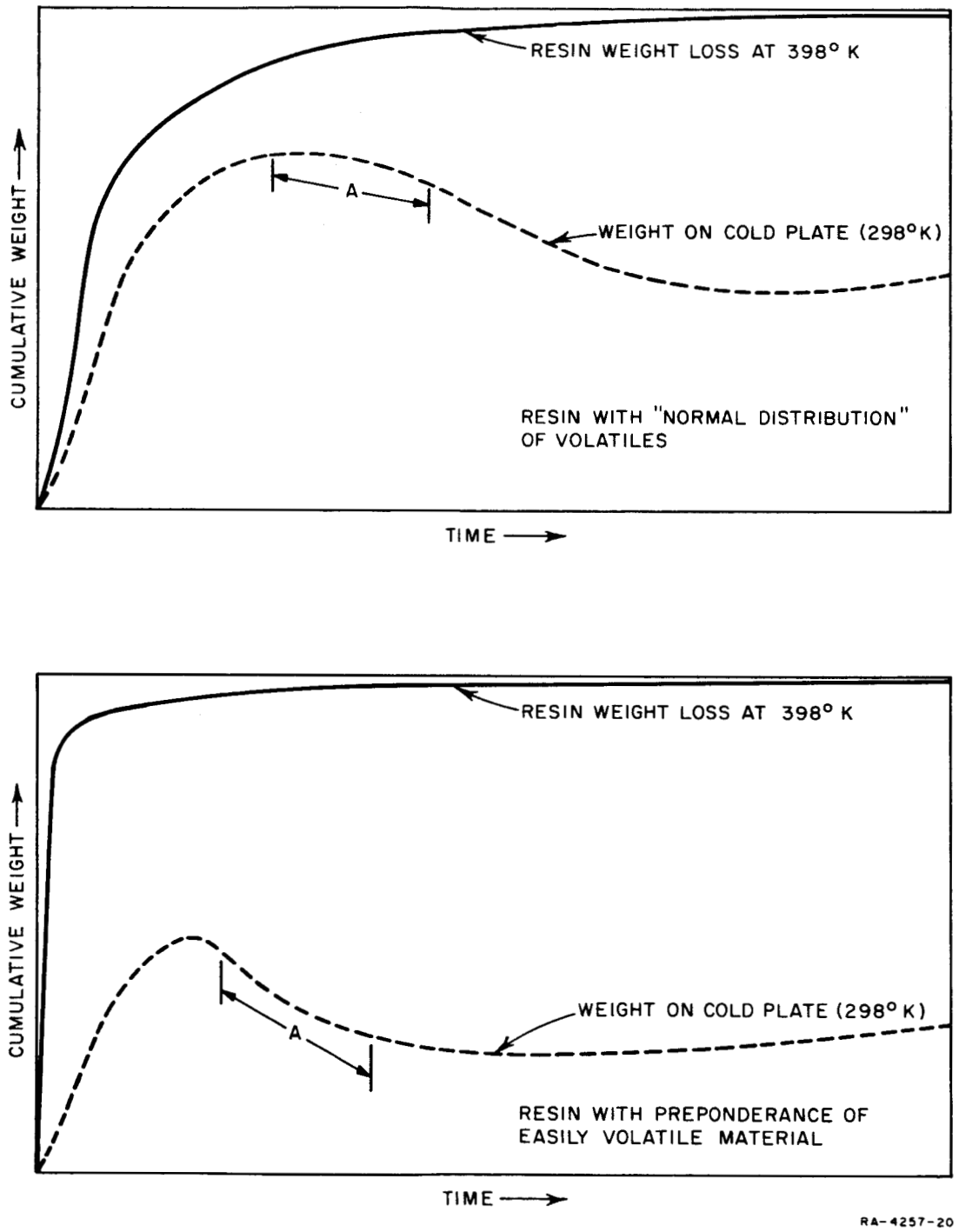


FIG. II-4 DIAGRAMMATIC REPRESENTATION OF THE QUALITATIVE RELATION OF LOSS OF WEIGHT OF RESINS AT 398°K TO VCM RESULTS

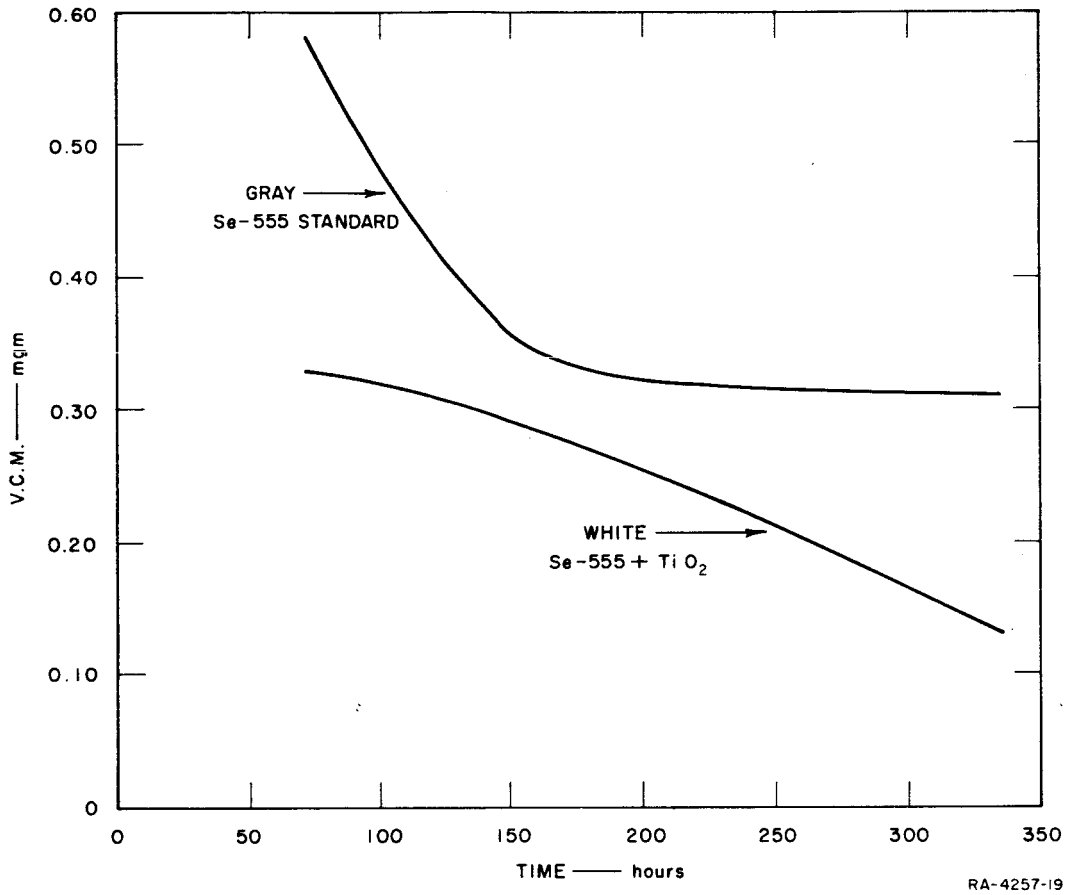


FIG. II-5 EFFECT OF VACUUM EXPOSURE TIME ON VOLATILE CONDENSABLE MATERIAL FROM GE SILICONE RUBBERS AT 125°C DEPOSITED ON 1"-DIAM SURFACE AT ABOUT 25°C

III. MASS SPECTROMETER STUDY OF POLYMERIC MATERIALS

J. S. Whittick

The purpose of the mass spectrometer studies was to determine the nature of the volatile material which is released by selected commercial polymeric substances in vacuum at a temperature of 125°C. Laboratory-prepared or -treated polymers were also studied to determine the effect of process variations on the release of volatile material.

The mass spectrometer employed in this work is a Consolidated Electrodynamic Corporation Model 21-103C, which is operated without a molecular leak to attain maximum sensitivity. A modified inlet system of small volume permits material vaporized from a polymer to travel a direct line-of-sight path into the ionization region; this inlet system is illustrated in Figure III-1. (A more detailed description of the mass spectrometer system is given in Interim Report No. 1.)

A general procedure for conducting the mass spectrometer studies has been established: A polymeric sample of the order of 20-40 mgm is weighed into a small tube which is then placed in the glass tube of the inlet system illustrated in Figure III-1. The system is evacuated, and after a period of one hour, when the analyzer pressure is about 5×10^{-6} mm of Hg, the first spectrum is recorded.

After 24 hours of evacuation at room temperature, the spectrum is again recorded (pressure about $2\text{-}3 \times 10^{-7}$ mm of Hg); if the characteristic instrument background spectrum is not indicated, evacuation is continued for another 24 hours.

When the sample has been completely degassed at room temperature, a small furnace is placed around the glass sample holder (Figure III-2). In about one hour, the temperature of the sample has been stabilized at 125°C, and the spectrum is recorded (this is the spectrum at "start time"). The spectrum of volatile material is then recorded every 24 hours until the spectrum is essentially the same as the expected instrument background; the run is then terminated, and the cold sample is weighed.

Generally, only traces of polymer constituents are apparent in spectra recorded after the first hour of evacuation at room temperature, and, for the most part, these traces disappear within 24 hours. The normal instrument background for the first hour of evacuation and subsequent times was determined by a "dry run" in which the entire procedure for cleaning, weighing, handling the sample tube, evacuating at room temperature, and operating at 125°C was duplicated.

Silicone Rubbers

Samples of several commercial silicone rubbers and two laboratory-compounded silicone rubbers have been studied in the mass spectrometer at a pressure of 10^{-7} mm of Hg and a temperature of 125°C. Critical examination of the mass spectra of the material released from the silicones under these conditions, and consideration of available information as to the chemical structure and compounding of silicones[1-4] indicate that no volatile material results from the decomposition or unzippering of the silicone rubbers themselves; any observable volatile matter is directly assessable to the release of extraneous products incorporated intentionally or accidentally during manufacture.

The commercial samples were provided by the Cognizant Engineer (JPL):

SE-555, standard	- GE silicone rubber (grey)
SE-555 + red iron oxide	- GE silicone rubber (red)
SE-555 + titanox	- GE silicone rubber (white).

Polymerization was reported to be catalyzed with 0.8 parts SG-50 (50% active benzoyl peroxide) and the polymers were post-cured 3 hours at 400°F; the nominal composition was indicated as SE-555 (methyl-phenyl-vinyl-polysiloxane) with Cab-O-Sil as a filler.

A laboratory-prepared silicone rubber was compounded by the SRI Polymer Group from a General Electric Co. base stock, SE-555U. A 50-g quantity of the base stock was milled on a 2-roll rubber mill with 0.4 g of benzoyl peroxide, introduced without addition of silicone oil. The material was then stripped and remilled six times to disperse the solid catalyst; a sheet approximately 1/2-inch thick was obtained. The sheet was cured for 3 hours

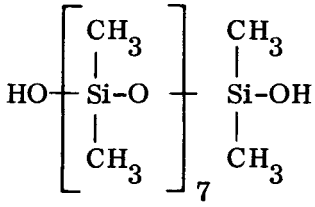
at 400°F in an oven. Cumyl peroxide was used as a catalyst in the compounding of a second, similar silicone rubber.

The composition of the volatile material released by each silicone as a function of exposure time is given in Tables III-1 to III-4. In all instances, the greatest production of volatile material occurs at start time (just as the sample is brought to 125°C) and, generally, the material released after 48 hours of exposure is essentially what is considered "trace" quantities in the usual mass spectrometric analysis.

Eleven species of silicon compounds have been identified in the material released initially and have been assigned relative per-cent values; these values have been calculated from the summation of "base" peak height for each identified component with an estimated peak height total for unidentified material. Part of the unidentified material occurs at m/e 18 which may be attributed to any or all of the following sources: (1) occluded water, (2) water of condensation, (3) water of fragmentation. Other unidentified peaks may well be rearrangement peaks (typical of Si-O compounds) which can not be correlated with a straightforward fragmentation pattern.

Possible origins for the various components are suggested:

(1)

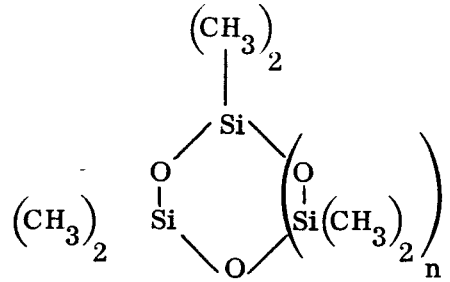


m.w. 759

This high-molecular-weight diol is a nonvolatile product of the hydrolysis of dimethyldichlorosilane; its formation is critically dependent on the quantity of water and the mutual solvent used for hydrolysis in the preparation of methyl silicone polymers. Such complex diols may be converted to volatile cyclic dimethylsiloxanes by thermal re-arrangement or pyrolysis[5,6].

(2) Cyclic dimethylsiloxanes are volatile products of the hydrolysis of dimethyldichlorosilane; they distill off at temperatures up to 200°C, with the

cyclic tetramer (n = 2) being the most volatile:

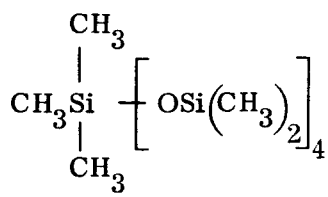


n = 1, 2, 3, 4, 5, 6, and 7

m.w. 222 to 666

Referring to Tables III-1 to III-4, it is seen that the cyclic dimethylsiloxanes are the smallest contributor (about 10%) to the volatile material released initially at 125°C in a vacuum. A striking contrast is noted after 24 hours when the cyclic dimethylsiloxanes now constitute as much as 75% of the volatilized material, and the diol (discussed above) essentially has disappeared. This immediately suggests that the environment in the mass spectrometer is conducive to the conversion of the diol to cyclic dimethylsiloxanes. Unfortunately, the mass spectra were recorded at intervals of 24 hours and no correlation (if any) can be made at this time between the time of the disappearance of the diol and the appearance of cyclic dimethylsiloxanes.

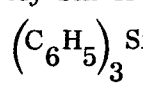
(3) The trimethylsilyl group is characteristically employed as a chain-blocker for silicone oils and greases. The low molecular weight fragment



m.w. 369

may have its origin in the silicone oil used to introduce the catalyst, but only 0.4 parts of the compounding mixture is a silicone oil; thus, it is perhaps more probable that the oil was inadvertently formed during the processing of the silicone polymer since $(CH_3)_3SiCl$ is one of the by-products which is either recirculated for further methylation or extracted purposely to prepare trimethylsilyl chain-blockers.

(4) The relatively small amount of triphenylsilanol,



m.w. 276

released initially at 125°C may result from the hydrolysis of $(C_6H_5)_3SiCl$ which is a recognized by-product from the preparation of silicones by the Grignard reaction and may well be one of the many by-products in the direct process.

(5) Although this compound, dimethyldiphenylsilane,

$$(CH_3)_2Si(C_6H_5)_2 \qquad \text{m.w. } 212$$

seems out of place in siloxane production, it is the only plausible assignment that can be made in the mass spectral pattern at the present time.

A summary of the mass spectrometer study of the volatile material from various silicone rubbers is given in Table III-5; also indicated are the relative quantities of volatile material produced by each silicone at start time and after 48 hours, when volatilization has reached a very low level. The weight loss of the silicones, incurred during their exposure to low pressure and high temperature in the sampling unit of the mass spectrometer, is included in this summary.

The silicone rubber compounded by the SRI Polymer Group with cumyl peroxide as a catalyst released at 25°C a mixture of siloxanes with molecular weights to 600. After 72 hours of pumping at 25°C, a mixture with molecular weights as high as 535 was still being released. Since most polymeric materials release little but common gases and water during the 25°C outgassing treatment, it was concluded that the material contained a large quantity of unpolymerized material, and the run was terminated.

The data in Table III-5 clearly indicate that the kind or the presence of additives (such as iron oxide or titanox) do not influence the composition of the volatile material.

Although the quantity of material released at start-time is highly variable, after 48 hours of exposure the same order of magnitude for each silicone is observed. One explanation for the initial variation in quantity of volatile material lies in the rapidity with which the material is released and pumped off at start time; any deviation in bringing the sample to an equilibrium 125°C can account for some variation. The noticeable reduction in the amount of volatile material released by the laboratory-compounded sample might be attributed to the introduction of twice the amount of catalyst as specified by General Electric.

It is interesting to note in Table III-5 that the disappearance of the dimethylsiloxane diol and triphenylsilanol together with the increase in cyclic dimethylsiloxanes is common to all the rubbers.

In view of the data given in Table III-5 and the above summary, it seems that the source of the volatile material lies primarily in the base stock used for compounding these silicone rubbers and that little volatile material is given off after 48 hours of exposure. Apparently, under conditions of 10^{-7} mm of Hg and 125°C, the silanol and the R_4Si are evaporated from the polymers, and the diol is converted into cyclic compounds which are gradually pumped off. The obvious procedure, then, was to pre-treat a bulk sample of a silicone rubber under conditions similar to those in the mass spectrometer study in order to determine the effect on volatile material production.

Because the General Electric SE-555 (standard product) released the greatest quantity of volatile material, a sample of this polymer was selected for pre-treatment. An 8-g piece of the rubber, 3/64" x 2-1/4" x 5", was maintained at 125°C in a vacuum desiccator (2×10^{-5} mm of Hg) for a period of 72 hours. The effect of this pre-treatment (or post-cure) was quite dramatic, as indicated in the last column of Table III-5. The quantity of diol was considerably reduced as expected, the ratio of cyclic polymers was increased, and the relative quantity of volatile material at start time was drastically reduced.

Further work on eliminating extraneous material from the silicone rubbers might be: (1) Determination of parameters of time and temperature for the most effective post-cure, (2) Determination of the quantity of material that can be effectively treated for special-purpose uses. It is doubtful that the removal of this small quantity of material would affect mechanical properties, but its presence may well create temporary problems of condensation on critical surfaces (see Section II).

6-Nylon

The results of a study of DuPont 6-nylon and a laboratory-prepared 6-nylon (see Interim Report No. 1) are given in Table III-7 and Table III-8. Both set of spectra indicated that the monomer, ϵ-caprolactam, was the only

constituent of the volatile material. The only difference between the two polymers was the tendency of the laboratory-prepared polymer to release a slightly larger quantity of monomer for a longer period of time.

Viton (vinylidene fluoride-hexafluoropropylene)

The composition of volatile material released by samples of Viton A and Viton B during their exposure to the vacuum-thermal environment of the mass spectrometer inlet system are given in Tables III-9 and III-10. The components of the volatile material are the same for either Viton; the ratios of components are the same at start time, but there is some difference in H_2O and CO_2 after 24 hours of exposure. The quantity of volatile material released by the Viton A is a little greater than Viton B, although both spectra after a 44-hour exposure period indicate instrument background.

The fact that HF (or free F combined with excess H_2O) is found in the volatile material released by the Vitons is not surprising; especially since investigations, e.g., Moore and Rau[7], have shown that Viton gaskets undergo thermal degradation in high-temperature water to release acidic fluorides which cause stress-corrosion cracking of structural alloys.

The HCl reported is apparently due to trace quantities of impurities in the co-polymers. A brief survey of several process for the manufacture of vinylidene fluoride indicated that one of the final steps requires the fluorination of chlorinated compounds.

Also indicated in the spectra are several fluorinated compounds with $-CH_2$ linkages. Since the quantity of this material was so small, no detailed attempt was made to identify the compounds.

Pip 2-U (laboratory-prepared polyurethane)

The mass spectrometer study of the Pip-2U is given in Section IV of this report.

Conclusions

The work performed thus far indicates that the mass spectrometer can be used effectively to determine whether "space grade" polymers decompose at a temperature of 125°C and vacuums better than 10^{-7} mm of Hg.

The polymers investigated are: Vitons A and B; GE silicone rubbers SE-555 standard, + TiO_2, + Fe_2O_3; 6-nylon; laboratory-prepared Pip-2U. With the possible exception of 6-nylon, none of the polymers gave indication of skeletal breakdown, but all of them gave off various materials which appeared to be impurities (other than N_2, CO_2, H_2O, etc.). Identification of most of the materials evolved from the polymers was possible.

Mass spectrometric results on heated polymers are necessary for correct interpretation of V. C. M. determinations (see Section II) and, in most instances, afford a more convenient index of the suitability of polymers for use in space.

TABLE III-1

MASS SPECTROMETER STUDY OF GE SILICONE RUBBER
SE-555, STANDARD PRODUCT

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material	
Start*	4×10^{-7}	$HO\left[Si\left(CH_3\right)_2O\right]_7 Si\left(CH_3\right)_2OH$	~30%
		$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~12%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$	~11%
		n = 3, 4, 5, 6, 7, 8, 9**	
		$\left(C_6H_5\right)_3SiOH$	~ 6%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~31%
		Miscellaneous	~10%
20 hours	3×10^{-7}	$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~24%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~71%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 5%
		Miscellaneous	~10%
45 hours	3×10^{-7}	$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~16%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~72%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 2%
		Miscellaneous	~10%

*Sample was degassed at 25°C, and then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table III-6.

TABLE III-1 (Cont'd)

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material	
92 hours	3×10^{-7}	$(CH_3)_3Si[OSi(CH_3)_2]_4$	~16%
		Cyclic $[OSi(CH_3)_2]_{n**}$	~72%
		$(CH_3)_2Si(C_6H_5)_2$	~ 2%
		Miscellaneous	~10%
164 hours	2×10^{-7}	$(CH_3)_3Si[OSi(CH_3)_2]_4$	~13%
		Cyclic $[OSi(CH_3)_2]_{n**}$	~75%
		$(CH_3)_2Si(C_6H_5)_2$	~ 2%
		Miscellaneous	~10%

*Sample was degassed at 25°C, and then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table III-6.

TABLE III-2

MASS SPECTROMETER STUDY OF GE SILICONE RUBBER
SE-555 + RED IRON OXIDE

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Components	
Start*	5×10^{-7}	$HO\left[Si\left(CH_3\right)_2O\right]_7 Si\left(CH_3\right)_2OH$	~27%
		$\left(CH_3\right)_3 Si\left[OSi\left(CH_3\right)_2\right]_4$	~13%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$	~ 7%
		n = 3, 4, 5, 6, 7, 8**	
		$\left(C_6H_5\right)_3 SiOH$	~ 6%
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	~37%
		Miscellaneous	~10%
55 hours	3.5×10^{-7}	$\left(CH_3\right)_3 Si\left[OSi\left(CH_3\right)_2\right]_4$	present
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$	not recorded
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	present

*Sample was degassed at 25°C, then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table III-6.

TABLE III-3

MASS SPECTROMETER STUDY OF GE SILICONE RUBBER
SE-555 + TITANOX

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Components	
Start*	4×10^{-7}	$HO\left[Si\left(CH_3\right)_2O\right]_7 Si\left(CH_3\right)_2OH$	~30%
		$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~12%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$	~11%
		n = 3, 4, 5, 6, 7, and 8**	
		$\left(C_6H_5\right)_3SiOH$	~ 5%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~32%
		Miscellaneous	~10%
24 hours	3.5×10^{-7}	$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~15%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~70%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 5%
		Miscellaneous	~10%
45 hours	3.5×10^{-7}	$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~16%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~71%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 3%
		Miscellaneous	~10%

*Sample was outgassed at 25°C, and then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table II-

TABLE III-3 (Cont'd)

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Components	
144 hours	3×10^{-8}	$(CH_3)_3 Si [OSi (CH_3)_2]_4$	~12%
		Cyclic $[OSi (CH_3)_2]_{n**}$	~76%
		$(CH_3)_2 Si (C_6H_5)_2$	~ 2%
		Miscellaneous	

*Sample was outgassed at 25°C, and then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table II-

TABLE III-4

MASS SPECTROMETER STUDY OF SILICONE RUBBER COMPOUNDED IN LABORATORY

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Components	
Start*	5×10^{-7}	$HO\left[Si\left(CH_3\right)_2O\right]_7 Si\left(CH_3\right)_2OH$	~27%
		$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~17%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~ 5%
		n = 3, 4, 5, 6, 7, and 8	
		$\left(C_6H_5\right)_3SiOH$	~ 6%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~35%
		Miscellaneous	~10%
23 hours	4×10^{-7}	$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~27%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~58%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 5%
		Miscellaneous	~10%
47 hours	3.5×10^{-7}	$\left(CH_3\right)_3\left[OSi\left(CH_3\right)_2\right]_4$	~20%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~68%
		$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~ 2%
		Miscellaneous	~10%

*Sample was degassed at 25°C, then raised to 125°C within one hour.
**Individual cyclic compounds are itemized in Table II-

TABLE III-4 (Cont'd)

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Components	
190 hours	3×10^{-7}	$\left(CH_3\right)_3 Si \left[OSi\left(CH_3\right)_2\right]_4$	~14%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~75%
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	~ 1%
		Miscellaneous	~10%

**Individual cyclic compounds are itemized in Table II-

TABLE III-5

MASS SPECTROMETER STUDY OF GE SILICONE RUBBER SE-555, STANDARD, DEGASSED*

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Components	
Start time**	3.5×10^{-7}	$HO\left[Si\left(CH_3\right)_2\right]_6 Si\left(CH_3\right)_2 OH$	~ 14%
		$\left(CH_3\right)_3 Si\left[OSi\left(CH_3\right)_2\right]_2$	~ 24%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n**}$	~ 34%
		n = 3, 4, 5, and 6	
		$\left(C_6H_5\right)_3 SiOH$	~ 2%
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	~ 16%
		Miscellaneous	~ 10%
23 hours	3×10^{-7}	$\left(CH_3\right)_3 Si\left[OSi\left(CH_3\right)_2\right]_2$	~ 17%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_{n***}$	~ 71%
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	~ 2%
		Miscellaneous	~ 10%
47 hours		$\left(CH_3\right)_3 Si\left[OSi\left(CH_3\right)_2\right]_2$	~ 16%
		Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$	~ 72%
		$\left(CH_3\right)_2 Si\left(C_6H_5\right)_2$	~ 2%
		Miscellaneous	~ 10%

*Degassing prior to mass spectrometer study is discussed in text.
**Sample was de-gassed in mass spectrometer at 25°C, and then raised within one hour to 125°C.
***Individual cyclic compounds are itemized in Table III-

TABLE III-6

SUMMARY OF MASS SPECTROMETER STUDY OF SILICONE RUBBERS

Identified Components	Silicone Rubbers Studied														
	SE-555, GE, standard			SE-555 plus iron oxide			SE-555 plus titanox			Lab-compounded			SE-555, standard degassed*		
	start	22 hrs	45 hrs	start	22 hrs	45 hrs	start	22 hrs	45 hrs	start	22 hrs	45 hrs	start	22 hrs	45 hrs
$HO\left[Si\left(CH_3\right)_2O\right]_7Si\left(CH_3\right)_2OH$	~30%	-	-	~27%		-	~30%	-	-	~27%	-	-	~14%	-	-
$\left(CH_3\right)_3Si\left[OSi\left(CH_3\right)_2\right]_4$	~12%	~24%	~16%	~13%		present	~12%	~15%	~16%	~17%	~27%	~20%	~24%	~17%	~16%
Cyclic $\left[OSi\left(CH_3\right)_2\right]_n$															
n = 3	~ 3%	~47%	~50%	~ 1%		not recorded	~ 4%	~50%	~54%	~ 2%	~42%	~51%	~23%	~58%	~61%
n = 4	~ 2%	~10%	~11%	~ 1%			~ 1%	~10%	~10%	< 1%	~10%	~11%	~ 6%	~13%	~11%
n = 5	~ 2%	~ 5%	~ 5%	~ 1%			~ 2%	~ 4%	~ 4%	< 1%	~ 5%	~ 4%	~ 3%	-	-
n = 6	~ 2%	~ 5%	~ 3%	~ 1%			~ 1%	~ 3%	~ 3%	< 1%	< 1%	~ 1%	~ 2%	-	-
n = 7	~ 1%	~ 3%	~ 2%	~ 1%			~ 1%	~ 3%	-	< 1%	< 1%	~ 1%	-	-	-
n = 8	~ 1%	~ 1%	~ 1%	~ 2%			~ 2%	-	-	~ 1%	-	-			
n = 9	< 1%	-	-	-											
$\left(C_6H_5\right)_3SiOH$	~ 6%	-	-	~ 6%		-	~ 5%	-	-	~ 6%	-	-	~ 2%	-	-
$\left(CH_3\right)_2Si\left(C_6H_5\right)_2$	~31%	~ 2%	~ 2%	~37%		present	~32%	~ 5%	~ 3%	~35%	~ 5%	~ 2%	~16%	~ 2%	~ 2%
Relative Quantities* (arbitrary units)	75.0	6.8	5.4	22.4		1.0	17.3	2.0	2.3	7.3	3.4	3.1	2.1	0.6	0.8
Weight Loss	0.78% (164 hours)			0.53% (55 hours)			0.65% (144 hours)			0.43% (190 hours)			0.18% (48 hours)		

*Based on summation of the base-peak heights of identified components with the total peak heights of unidentified components (contributing not more than 10% to the total value); quantity of evolved material is proportional to peak heights.

TABLE III-7

MASS SPECTROMETER STUDY OF 6-NYLON
(DUPONT)

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material
Start*	4.5×10^{-7}	99+ % ϵ-caprolactam
42 hours	3.0×10^{-7}	same
490 hours	2.0×10^{-7}	same

*Sample was outgassed at 25°C, heated for a short period at 50°C, and then raised to 125°C.

TABLE III-8

MASS SPECTROMETER STUDY OF 6-NYLON
(LABORATORY-PREPARED)

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material
Start*	5.5×10^{-7}	99+ % ϵ -caprolactam
46 hours	3.8×10^{-7}	same
118 hours	3.0×10^{-7}	same

*Sample was outgassed at 25°C, heated for a short period at 50°C, and then raised to 125°C.

TABLE III-9

MASS SPECTROMETER STUDY OF VITON A*

Sample weight: 36.144 mg
Weight loss: 0.24%

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material		
Start**	6.5×10^{-8}	H_2O	~	94%
		CO_2	~	3%
		HCl	~	1%
		$H_nC_nF_n$	~	1%
		HF	<	0.5%
27 hours	3.5×10^{-8}	H_2O	~	77%
		CO_2	~	9%
		$H_nC_nF_n$	~	8%
		HCl	~	2%
		HF	<	3.5%
70 hours	3.0×10^{-8}	Traces of fluorocarbons		

*DuPont -776; a co-polymer of vinylidene fluoride and hexafluoropropylene.
**Sample was outgassed 24 hrs at 25°C and then raised to 125°C within 1 hour.

TABLE III-10

MASS SPECTROMETER STUDY OF VITON B*

Sample weight: 27.907 mg
Weight loss: 0.15%

Exposure at 125°C	Analyzer Pressure mm of Hg	Identification of Volatile Material		
Start**	6×10^{-8}	H_2O	~	91%
		CO_2	~	5%
		$H_nC_nF_n$	~	1%
		HCl	~	2%
		HF	<	0.5%
20 hours	4×10^{-8}	H_2O	~	67%
		CO_2	~	24%
		$H_nC_nF_n$	~	4%
		HCl	~	3%
		HF	~	2%
44 hours	4×10^{-8}	(same as 20 hours)		

*DuPont-778; a co-polymer of vinylidene fluoride and hexafluoropropylene.
**Sample was outgassed 24 hrs at 25°C and then raised to 125°C within 1 hour.

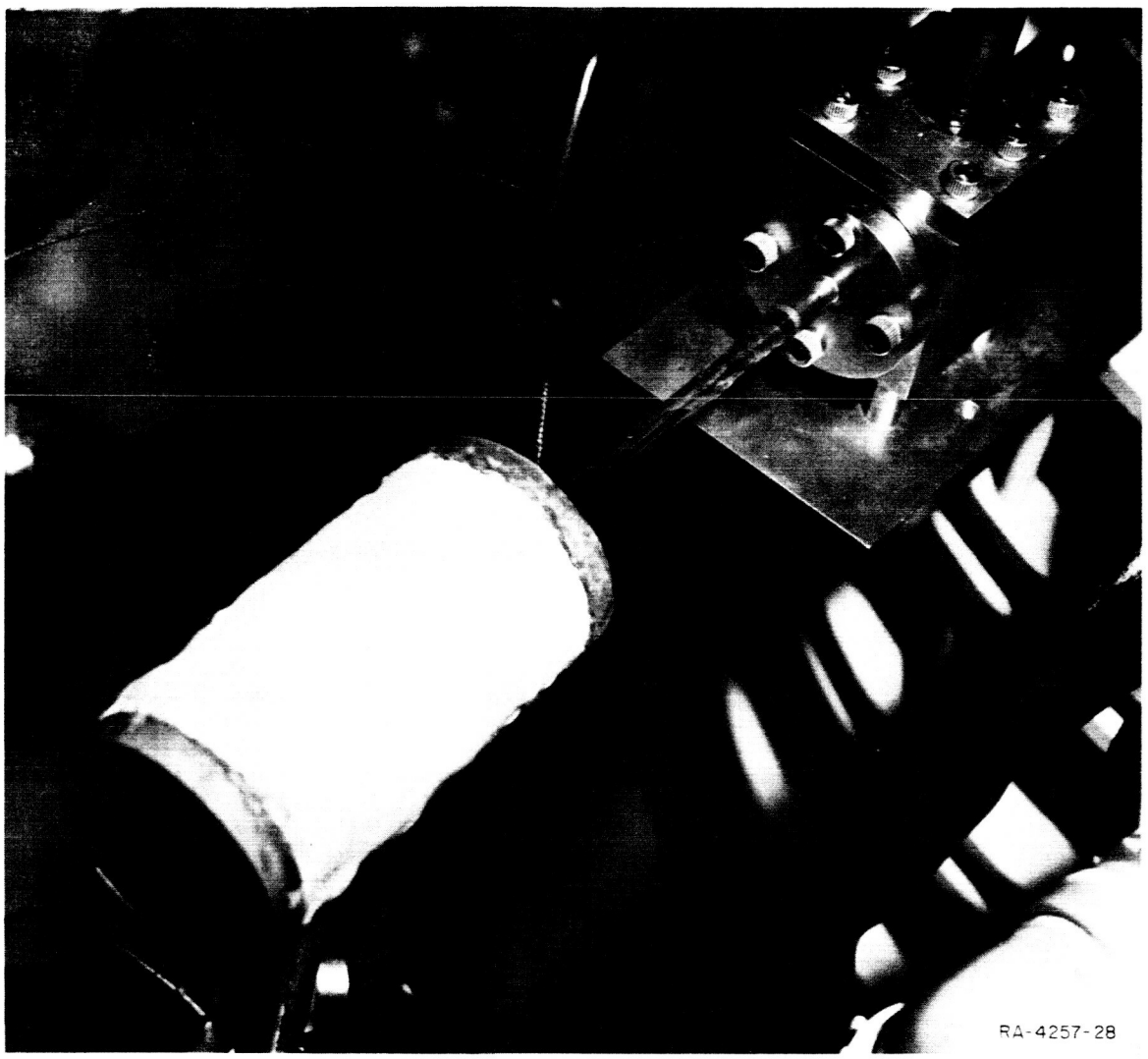


FIG. III-1 VIEW OF MODIFIED MASS SPECTROMETER INLET SYSTEM SHOWING SAMPLE TUBE IN PLACE

FIG. III-2 VIEW OF MODIFIED MASS SPECTROMETER INLET SYSTEM SHOWING FURNACE IN PLACE AROUND SAMPLE TUBE

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IV. POLYMER SYNTHESIS AND DEGRADATION STUDIES

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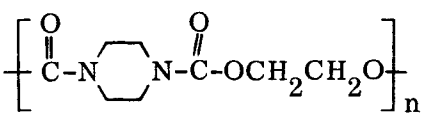
The determination of the mechanisms of chemical degradation of polymeric materials subjected to high vacuum and elevated temperature was one of the objectives of this program of work. Two types of polymers have been selected for extensive study: (1) polyamide and (2) polyurethane. The work has involved the syntheses of polymers and exploratory work on the degradation of the synthesized polymers.

Although many reports have been published concerning the effects of temperature, pressure, and impurities upon the degradation process of nylon polymers, no unequivocal mechanism can be derived from this information. The synthesis of nylon polymers tagged with deuterium at likely points of initial bond breaking was undertaken in order to enhance the study of primary degradation mechanisms. Chosen as a model structure for deuterium studies was 6-nylon because it has a simple structure, because it is one of the commercially prominent nylon materials, and because deuteration of the precursor compounds appeared to be more readily accomplished than for other nylon structures.

In 6-nylon, $\left[\mathrm{N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(=O)}\right]_n$ (positions 1 2 3 4 5 6 7), there are six positions at which hydrogen may be replaced by deuterium. Certain of these positions will play a much more important role in degradation processes than others; however, H-D exchange is difficult at some of these positions. A consideration of possible degradation mechanisms and of synthesis problems led to the choice of positions 1[6-nylon-1d], 2[6-nylon-2, $2d_2$], and 4[6-nylon-4, $4d_2$] for preliminary work, and positions 2 and 6[6-nylon-2, 2, 6, 6, d_4] for extended work.

The polyurethane from piperazine

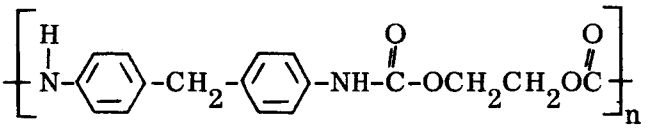


(pip-2U)

was selected for study because the ring structure of the diamine prevents the formation of a diisocyanate on degradation, thereby preventing additional side

reactions which may mask the basic degradation mechanism occurring in the ester portion of the urethane. The possibility of application of data obtained from the degradation studies of polyethylene terephthalate,[1-6] which is a structural analog of pip-2U, also influenced this selection.

A polyurethane based on methylene (bis)aniline and ethylene glycol



(pip-2U)

was selected for the study of the contribution to the degradation mechanism by the amide portion of the urethane linkage. The two amino groups of this structure are essentially equivalent in their reactivity and therefore do not introduce any rate or steric effects, while the ester portion is similar to pip-2U. In addition, the pip-2U represents a molecular structure equivalent to that found in commercial polyurethanes.

6-Nylon

2-Oxohexamethylenimine (ϵ-caprolactam, Matheson, Coleman, and Bell) was twice recrystallized from purified cyclohexane and polymerized under nitrogen, with water as a catalyst, according to the procedure of Sorenson and Campbell.[7]

The milky-white polymer had an inherent viscosity of 0.96 in m-cresol at 30°C.

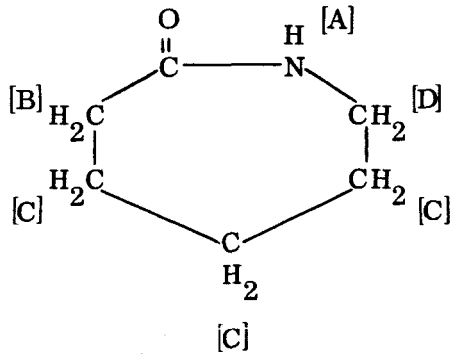
6-Nylon-1d

2-Oxohexamethylenimine-1d. In a typical preparation, 11.3 g (0.10 mole) of recrystallized 2-oxohexamethylenimine was stirred at room temperature with 2.0 g (0.1 mole) of D_2O, in the presence of a catalyst, until equilibrium between OH and OD in the water phase was established. The imine was recovered and the exchange process was repeated until the rate of exchange became impractically small. The resulting product had deuterium content 85% of the theoretical value; exchange occurred only on nitrogen.

The evaluation of a series of catalysts indicated that basic catalysts were more effective than acidic catalysts in promoting exchange between NH groups and D_2O and that the most effective catalyst, in consideration of both rate and degree of exchange, was sodium deuteroxide. None of the catalysts, even when used in refluxing dioxane (which gave a homogeneous solution at a higher temperature than boiling cyclohexane) resulted in exchange with the hydrogen on the no. 7 carbon atom (α-to the carbonyl group) of 2-oxohexamethylenimine.

The deuteration reaction of 2-oxohexamethylenimine was followed by analyzing the infrared spectra of the cyclohexane-H_2O azeotrope distilled from the reaction mixture: comparison was made of the area under the OH peak at 2.9μ to the area under the OD peak at 3.9μ. This method of determining the OD-OH ratio was accurate within 2% on known mixtures of H_2O and D_2O.

Analyses of purified imine for deuterium content was made by both infrared spectroscopy and nuclear magnetic resonance spectroscopy; the results of the two methods agreed within 2-3%. In the infrared spectrum, the ratio of the area under the NH peak at 3μ to the area under the ND peak at 4μ [8] provides a measure of the extent of conversion. Since the 2-oxohexamethylenimine molecule has four nonequivalent sets



of hydrogen atoms, four distinct peaks are found in the NMR spectrum. As the H atoms at (A) are replaced by deuterium atoms, the area under the peak for the atoms at (A) diminishes. The decrease in area of this peak with respect to the area of any one of the other peaks also provides a quantitative measure of the concentration of N-D groups.

6-Nylon-2, $2d_2$

Attempts were made to synthesize 6-nylon-2, $2d_2$ via the following steps:

$$N{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow[\text{suitable D source}]{\text{reduction with}}$$

I

$$D_2N\text{-}CD_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \xrightarrow[H^+]{\text{hydrolysis}}$$

II

$$Cl^-\overset{+}{H}_3N\text{-}CD_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \xrightarrow[\text{polymerization}]{\text{interfacial}}$$

III

$$\left[\begin{array}{l} H \\ N\text{-}CD_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-} \end{array}\right]_n$$

ω-Cyanovaleramide [I] was prepared by the method of Wiley and Morgan.[9] Reduction of [I] to ω-amino-caproamide [II] was attempted with hydrogen prior to reduction with the expensive deuterium. No reduction occurred with platinum catalyst and H_2 gas at 60 psig in absolute ethanol or in glacial acetic acid. Reduction with rhodium catalyst in absolute alcohol, under a variety of conditions, yielded only secondary amine, or a hygroscopic mixture from which no primary amine could be isolated. Reduction with sodium in ethanol gave an intractable, very hygroscopic material.

6-Nylon-2, 2, 6, $6d_4$

Cyclohexanone-2, 2, 6, $6d_4$. In a typical preparation, 39.2 g (0.4 mole) of freshly distilled cyclohexanone, 8 ml (0.4 mole) D_2O, 30 ml dioxane, and 0.39 g (1.0 % based on cyclohexanone) of solid NaOH were placed in an 100-ml round-bottom flask. The flask was fitted with a reflux condenser and the reaction mixture was then gently refluxed. The rate of equilibration was followed by determining the ratio of H_2O and D_2O in the water-cyclohexanone azeotrope via infrared spectroscopy. The D_2O-H_2O mixture was removed about once each 24 hours and replaced by fresh D_2O. After 215 hours, and 9 D_2O additions, the cyclohexanone was recovered and distilled. NMR analysis showed that 93.3% of the 4 hydrogens in the 2 and 6 positions had been replaced by deuterium atoms. Combustion analysis for deuterium gave a value of 89.0%, and infrared analysis gave no consistent value for deuterium content of this cyclohexanone.

Cyclohexanoneoxime-2, 2, 6, $6d_4$. Cyclohexanone-2, 6, $6d_4$ (10.2 g, 0.10 mole) was converted to the oxime according to the method of Bosquet.[10] The method was modified by the addition of 10 ml of ethanol, which prevented the reaction mixture from caking. The product was recrystallized from water. Yield: 6.8 g (58%); m.p. 88.5-89.0 °C.

2-Oxohexamethylenimine-3, 3, 7, $7d_4$. Cyclohexanone-2, 2, 6, $6d_4$ was prepared by the method of Donaruma and Heldt,[11] using 98% sulfuric acid. The yield of crude product was 86%. After one recrystallization from cyclohexane, the melting point of the product was 70.4-70.6 °C. Analysis for deuterium by combustion, 89.0%, and by NMR, 90%.

Degradation Studies

The vacuum system used for the nylon degradation studies employs a CVC MCF-300 diffusion pump and a Welch Duo-Seal Model 1402 forepump. Pressure is monitored by a CEC GPH-100A Phillips gage; preliminary measurements have indicated a pressure of $< 10^{-7}$ mm of Hg, after a pump-down and bake-out period of 5 hours. A Toepler pump and gas burette were installed in the system in order to collect and measure noncondensable gases; the measurement and analysis of the condensable material and noncondensable gases will permit the calculation of a mass balance for the products of degradation.

The results of a preliminary degradation experiment, carried out on nondeuterated 6-nylon, are given in Table IV-1. An accumulated weight loss of 11.6% was incurred by the polymer during this experiment. The major volatile components accounting for the weight loss are water, carbon dioxide, and unidentified hydrocarbons; minor components are nitrogen and/or carbon monoxide, hydrogen, and oxygen. A negligible amount of noncondensable gases was found in a Toepler pump sample of the diffusion-pump exhaust.

POLYURETHANE SYNTHESES AND DEGRADATION STUDIES

Polymerizations

Polymers were prepared by solution polymerization techniques[12] and by interfacial polycondensation techniques.[13, 14] All chemicals were purified by classical methods.

Pip-2U. The polyurethane from piperazine was prepared by adding a solution of 9.35 g (0.05 mole) of ethylene bis(chloroformate)[15] in 30 ml of anhydrous dichloromethane to a rapidly stirred solution of 4.3 g (0.05 mole) piperazine and 10.6 g (0.10 mole) sodium carbonate in 100 ml of water in a Waring Blendor. The reaction mixture was stirred for 8 minutes, then poured into 500 ml of water, and the excess dichloromethane was evaporated on a steam bath. The polymer was filtered, washed with water and acetone, and dried in a vacuum oven at 80°C. The yield was 7.85 g (78%). Inherent viscosity was 0.94 in formic acid at 30 °C (conc. = 0.5 g/100 ml solution.)

Pip-2U. The polyurethane from methylene bis(aniline) was prepared as follows: 40 ml of 4-methylpentanone-2 and 25.02 g (0.10 mole) of methylene bix(4-phenyl isocyanate) were placed in a three-necked, round-bottom flask equipped with a stirrer and condenser and protected from moisture. To the rapidly stirred suspension was added a solution of 6.2 g (0.01 mole) of ethylene glycol in 40 ml of dimethyl sulfoxide. The reaction mixture was heated at 115°C for 1-1/2 hours. The resulting clear, viscous solution was then poured into water to precipitate the polymer. The tough, white polymer was shredded in a home blender, washed with water and acetone, and dried in a vacuum oven at 90°C. The inherent viscosity was 0.56 in N, N-dimethylformamide at 30°C.

Polymer Degradation Procedures

Two series of degradations were carried out on each polyurethane; the first involved thermal-vacuum degradation at various temperatures of thin films cast on salt plates. (Films of the polyurethane based on piperazine were cast from dichloromethane, while those of the polyurethane based on methylene dianiline were cast from N, N-dimethylformamide.) Infrared spectra of the

films were recorded on a Perkin-Elmer Model 221 spectrophotometer before and after each thermal-vacuum cycle.

In the second series, larger samples (ca. 1-2 g) of the polymer were degraded under comparable thermal-vacuum conditions. Gaseous products were collected in a liquid nitrogen trap and then transferred to an evacuated 10-cm infrared cell in order to record the spectrum. The contents of the cell were then transferred to an U-tube cooled in liquid nitrogen, and subsequently were analyzed by vapor-phase chromatography using a 5-foot 20% TCEP on Chromosorb P column operated at room temperature. Mass spectrometric analyses were performed on duplicate runs; in this instance, contents of the liquid nitrogen trap were transferred directly into a Consolidated Engineering Corporation mass spectrometer, Model 21-103C. In addition, the piperazine polymer was degraded directly in a mass spectrometer system (vide infra).

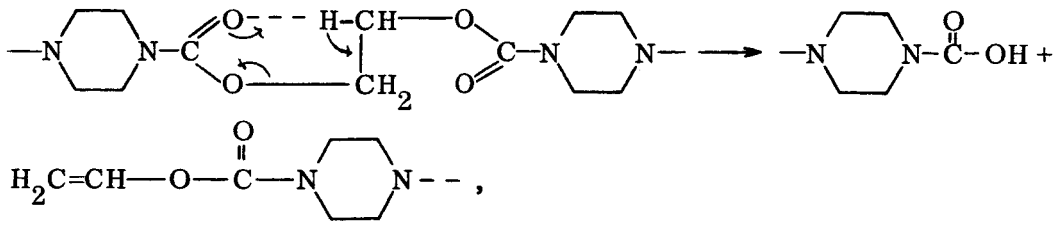
All polymers were degassed 12 hours before degradation experiments were started, and degradation temperature was controlled by vapor baths. Pertinent data from the degradation experiments are summarized in Table IV-2.

Degradation of Pip-2U

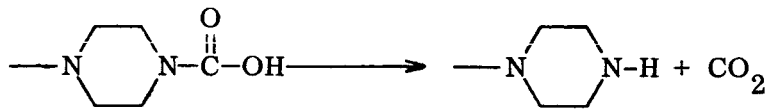
The polyurethane, pip-2U was found to be resistant to degradation under thermal-vacuum conditions of temperatures ranging from 25 to 222°C and pressures ranging from atmospheric to 10^{-7} mm of Hg. There were no detectable changes in the infrared spectra of films other than loss of absorption bands of the solvent, CH_2Cl_2; solvent loss was confirmed in an experiment where the polymer was degraded directly in the mass spectrometer system. In the mass spectrometric degradation at higher temperatures, i.e., 175-222°C, it was found that low-molecular-weight species, primarily cyclic dimer and some piperazine, distilled from the sample. However, since the presence of these species diminished with time, they were not considered products of the breakdown of high-molecular-weight polymer chains.

Degradation of the polymer at 225°C in the mass spectrometer was indicated by a shift in peak ratios and the gradual disappearance of the dimer fragmentation pattern. At 250°C, a degradation product of apparent mass 344 was evident. The effect of temperature on the polymer was substantiated

in separate experiments in which the infrared spectra of films of the polymer first showed changes at 242°C and continual shifts of patterns at 255°C. Volatile products from the film degradations were identified as being primarily CO_2, with small quantities of ethylene oxide and acetaldehyde. The evolution of CO_2 coupled with the rapid decrease in viscosity of the polymer indicates that the major initial degradation reaction is an alkyl-oxygen scission,

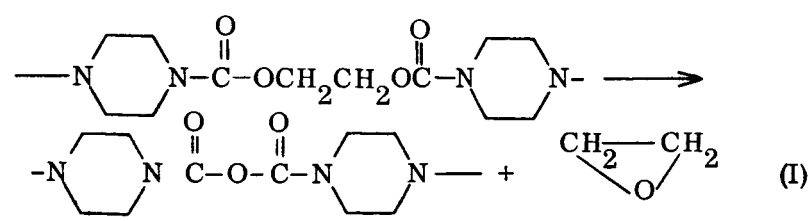
(1) 

followed by a decarboxylation of the carbamic acid derivative,

(2) 

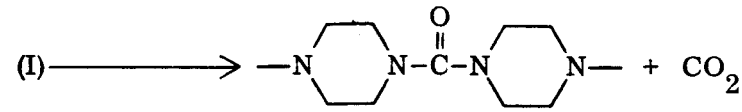
This has been confirmed by the presence of both -NH and CH=CH- absorption bands in the infrared spectra of the degraded polymer residue. In general, the strong absorption bands associated with the urethane linkage diminished at 242°C and three new bands appeared: 2.9μ ($\geq$ N-H): 6.05μ (C=C); and 6.1μ ($\geq$N-C(=O)-N$\leq$); the spectrum is shown in Figure IV-1. At 255°C, these changes were much more severe, although the N-H band at 2.9μ was not as pronounced.

The presence of small amounts of ethylene oxide and acetaldehyde in the volatile products of degradation, the observation that the polymeric residue reaches a more-or-less limiting viscosity value, and confirmation of the presence of urea structures by infrared absorption indicate that several addition reactions are concurrent with the alkyl-oxygen scission reaction. A possible route to the formation of ethylene oxide is a disproportionation of the urethane to the anhydride, thus causing formation of ethylene oxide:

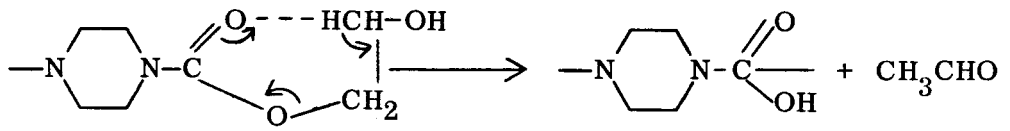
(3) 

(I)

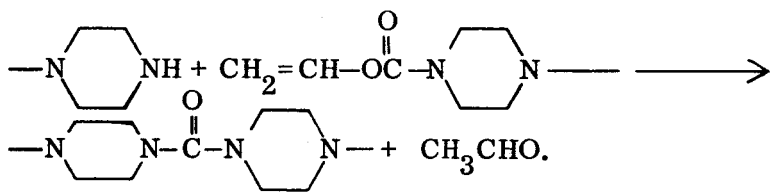
Examination of molecular models indicates that a configuration conducive to such a degradation is indeed possible. The anhydride formed in this reaction would be expected to break down further to give CO_2 and a urea,

(4) 

The presence of acetaldehyde in the volatile products might be attributed to the presence of $-OCH_2CH_2OH$ ends in the polymer chains. An alkyl oxygen scission at this location would lead to the formation of acetaldehyde:

(5) 

Another route to the formation of aceteldehyde would result from an aminolysis of the vinyl ester:

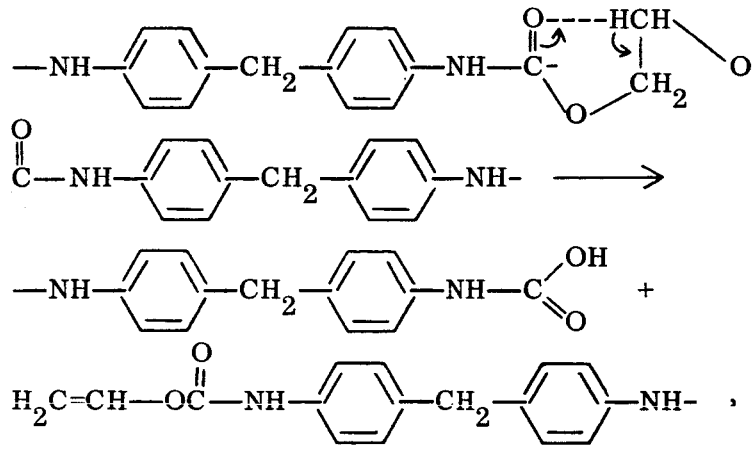
(6) 

Degradation of P1p-2U

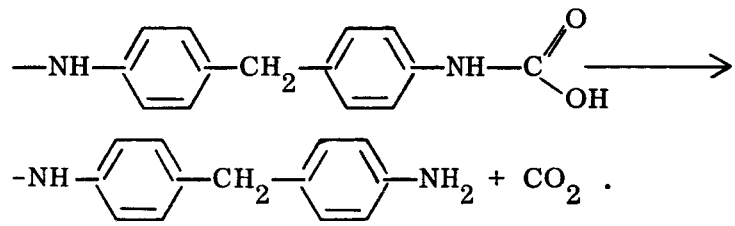
Once the mechanism of degradation of the ester portion of the urethane linkage was established, it was of interest to investigate the contribution of the amide portion of the urethane linkage which is typical of commercial polyurethanes. Degradation of the p1p-2U under thermal-vacuum conditions began at a lower temperature than that found for the piperazine-based polymer (160^{o} vs 225^{o}). Up to 160°C, the only change in the infrared spectra of p1p-2U was that due to loss of solvent (N, N-dimethylformamide) from which the film had been cast. On heating the film to temperatures of 179°C or greater, gross degradation took place and a crosslinked residue was obtained. The intense infrared absorption bands associated with the urethane linkage diminished and a new series of bands developed; the spectrum is shown in Figure IV-2.

The volatile products from the degradation, identified by mass spectrometry, showed CO_2 as the major product, with amounts ranging from 92% at 179°C to over 99% at 222-250°C. This evolution of CO_2 would also result from an alkyl-oxygen scission occurring in the ester segment of the polymer chain,

(9)

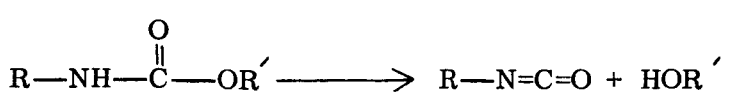


followed by a decarboxylation of the carbamic acid derivative:

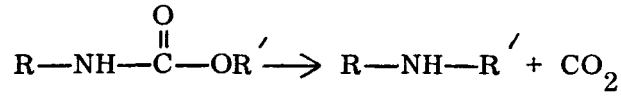


The facts that a smaller total quantity of CO_2 is evolved from this polyurethane than from pip-2U, and that the residue is highly crosslinked indicate that a competing degradation mechanism is minimizing the extent of alkyl-oxygen scission. Since the pip-2U is based on a primary amine, additional degradation and condensation routes are possible. These reactions would ultimately lead to a crosslinked product, and, as indicated above, could mask or prevent some of the degradations shown by the piperazine polymer. Of primary importance is the thermal decomposition of this urethane to the isocyanate and the alcohol. In special cases, this decomposition has been used as a preparative method for isocyanates:

(10)



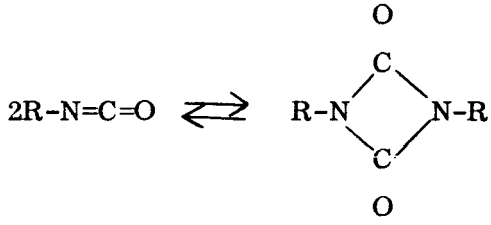
Another thermal decomposition which has been reported results in the formation of secondary amine, but little information is available on the extent to which this reaction may occur:



The isocyanate produced in the above thermal decomposition is quite reactive and can undergo many reactions leading to linear and crosslinked products.

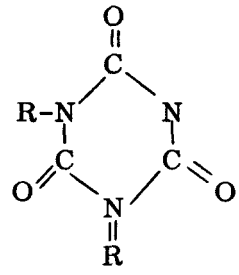
The formation of isocyanate dimer is not probable at the temperature involved in the degradation of the polyurethanes, since dissociation usually occurs at temperatures greater than 150°C:

(11)



However, formation of trimer is indeed possible,

(12)



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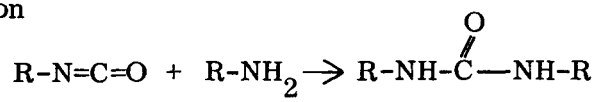
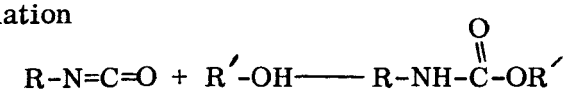
especially at temperatures from 150-200°C. The degradation of a polyurethane based on tetramethylene glycol and tetramethylene diamine did yield a triazine polymer. Infrared spectra of the films, however, showed no indication of a triazine structure.

The isocyanate could also react with any amine formed in the alkyl-oxygen scission or recombine with the alcohol to give a urea or urethane linkage, respectively,

(13) urea formation

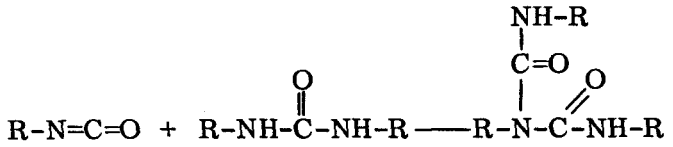


(14) urethane formation

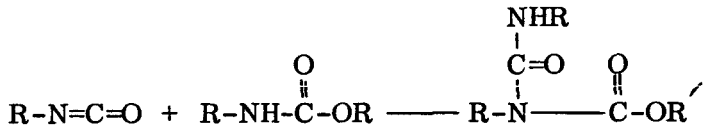


In addition, the isocyanate could react with the active hydrogens of the urea or urethane to give rise to biurets and allophanates which would result in crosslinked polymer. These reactions are of particular importance above 100°C:

(15) Biuret formation



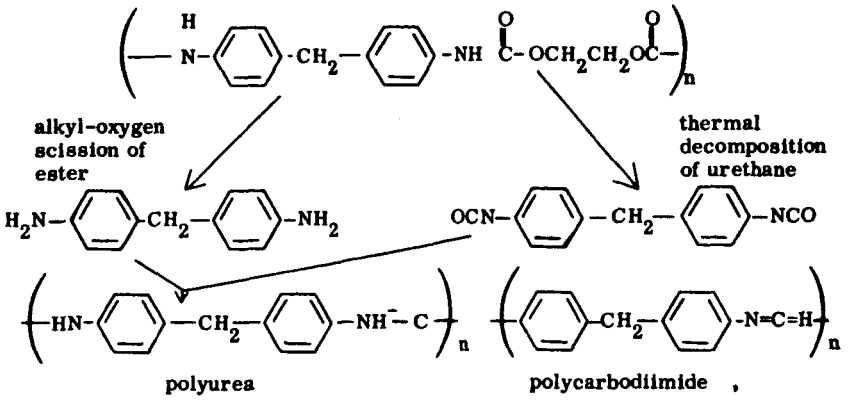
(16) allophanate formation



In general, the ureas are more reactive than the urethanes, but greater concentration of the urethane linkages may be sufficient to overcome this.

This general mechanism of degradation is confirmed by the production of the insoluble cross-linked product as well as by the infrared spectra which indicate urea, biuret, and allophanate absorptions.

The sublimates also conform both the basic amide and the basic ester degradation of the polyurethanes for these products are a mixture of those expected from both decomposition routes. Both the polyurea and the polycarbodiimide have been identified by comparison with, e.g.,



the corresponding synthesized structure.[16] It is of interest that the carbodiimide linkage was only detectable in the sublimates and was notably absent in the residue. This is in contrast to degradations carried out at 180-300 ^{o}C at atmospheric pressure.[17] Apparently, vacuum conditions have minimized this reaction in the bulk sample.

TABLE IV-1

VACUUM-THERMAL DEGRADATION OF 6-NYLON
(PRELIMINARY EXPERIMENT)

Exposure		Final System Pressure mm of Hg	Weight Loss of Sample	Accumulative Weight Loss
Time	Temp			
5 hrs	25^{o}C	2×10^{-6}	2.6%	2.6%
2 hrs	100^{o}C	2×10^{-5}	5.0%	7.6%
4.5 hrs	140^{o}C	1×10^{-5}	4.0%	11.6%

TABLE IV-2

DEGRADATION OF POLYURETHANES UNDER THERMAL-VACUUM CONDITIONS

Polymer	Wt	η_{inh}[(a)]		Wt	η_{inh}[(a)]	Sublimate	Volatiles CO_2	Volatiles 	Volatiles CH_3CHO	Remarks
pip-2U	1.150 g	0.94 (HCOOH)	$255^{o}C/2x10^{-2}$ mm Hg, 6 hrs	1.054 g	0.45 (HCOOH)		90.7%	– 9.3% – (b)		residue sol. in CH_2Cl_2
pip-2U	0.958 g	0.94 (HCOOH)	$255^{o}C/2x10^{-4}$ mm Hg, 6 hrs	0.81 g	0.49 (HCOOH)	Trace of dimer	99.9%	– 0.1% – (b)		residue sol. in CH_2Cl_2
pip-2U	1.000 g	0.46 (HCOOH)	$255^{o}C/2x10^{-5}$ mm Hg, 11 hrs	0.850 g	0.39 (HCOOH)	Trace of dimer	 ratio approx. 4.6/1. (c)			residue sol. in CH_2Cl_2
pip-2U	2.000 g	0.46 (HCOOH)	$255^{o}C/2x10^{-5}$ mm Hg, 12 hrs	1.740 g	0.38 (HCOOH)	Trace of dimer	 ratio approx. 5.4/1. (c)			residue sol. in CH_2Cl_2
p1p-2U	0.85 g	0.56 (DMF)[(d)]	$179^{o}C/2x10^{-4}$ mm Hg, 15 hrs	0.75 g	-		99.8%	– 0.2% – (b)		residue insol. DMF
p1p-2U	0.92 g	0.56 (DMF)[(d)]	$222^{o}C/2x10^{-4}$	0.60 g	-	polyurethane	99.6%	– 0.4% – (b)		residue insol. DMF
p1p-2U		0.56 (DMF)[(d)]	$255^{o}C/2x10^{-4}$ mm Hg, 6 hrs	0.48 g	-	methylene dianiline polyurethane polyurea polycarbodiimide	99.7%	– 0.3% – (b)		residue insol. DMF

(a) η_{inh} = inherent viscosity

(b) Volatiles identified by mass spectrometer to m/e 86.

(c) Volatiles identified by gas-liquid chromatography and infrared spectoscopy.

(d) DMF = N, N-dimethylformamide

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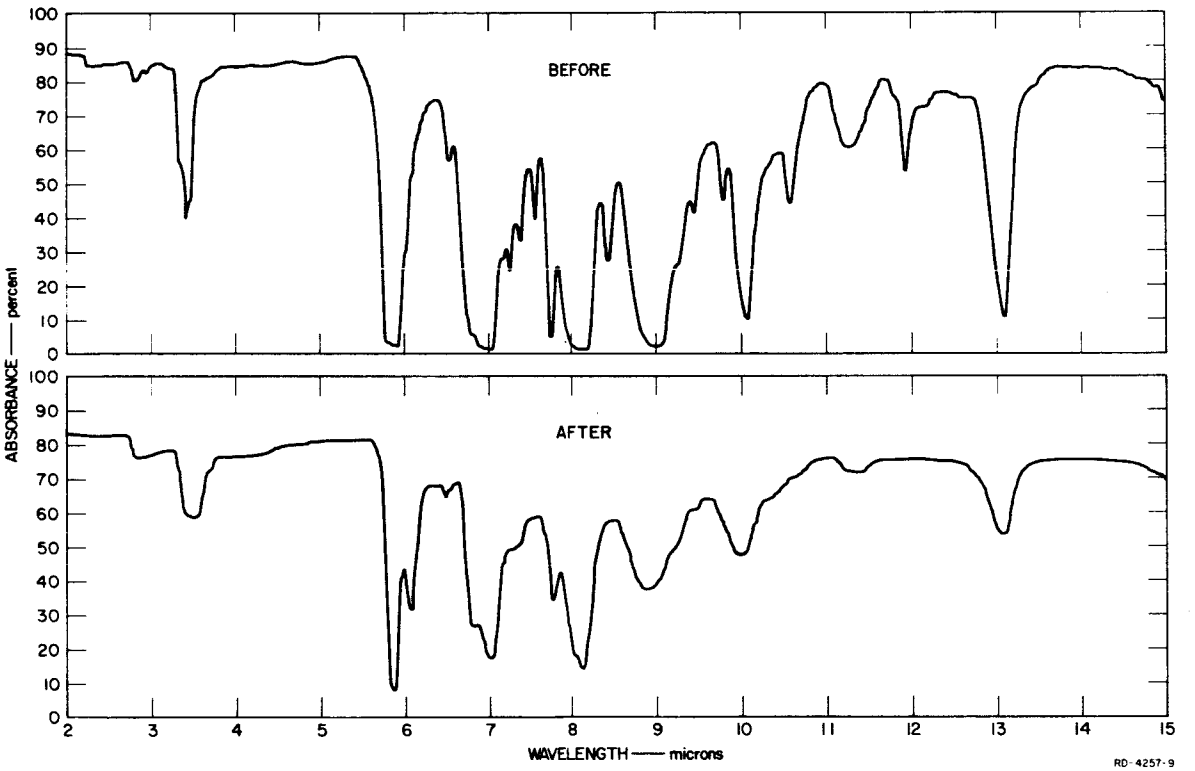

FIG. IV-1 INFRARED SPECTRA OF THE POLYURETHANE BASED ON PIPERAZINE:
(a) Original Polymer; (b) Degraded Polymer

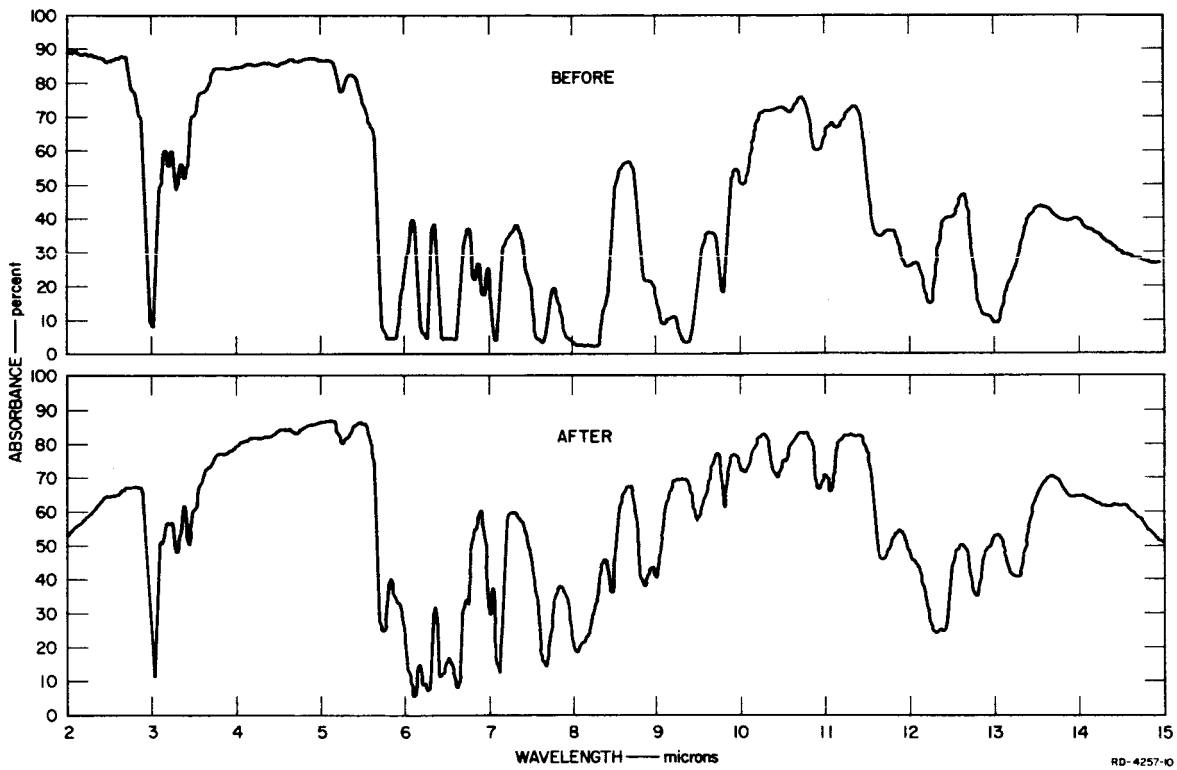

FIG. IV-2 INFRARED SPECTRA OF THE POLYURETHANE BASED ON METHYLENE DIANILINE; (a) Original Polymer; (b) Degraded Polymer

V. MECHANICAL PROPERTIES

L. D. Christensen

The objective of this phase of the program was to determine the effect of a vacuum-thermal environment on selected mechanical properties of candidate elastomers and plastics.

Three means for studying mechanical properties were employed: (1) continuous and intermittent stress relaxation, (2) creep at constant load, and (3) tensile properties at constant strain rate. The polymers tested were maintained at 125°C for periods up to 850 hours in vacuum; some of the samples were tested while in vacuum and other were later conditioned in air at 125°C, and tested in tension on the Instron tester.

Equipment was constructed to perform identical long-term tests on the polymers in air and in an inert environment. Thus, the results obtained in a vacuum-thermal environment are able to be correlated with the mechanical properties of new polymer samples and the mechanical properties measured on samples aged in air and in an inert atmosphere at the same test temperature.

The materials which have undergone testing during the present contract period are Viton A (DuPont A4411A-776), Viton B (DuPont A4411A-778), silicone rubber (General Electric, SE-555 + red iron oxide), Teflon TFE (DuPont), Teflon FEP-100 (DuPont), and Mylar film (DuPont, A100 and A200).

EXPERIMENTAL METHODS AND RESULTS

Continuous and Intermittent Stress-Relaxation Measurements

The vacuum-thermal stabilities of Viton B, Viton A and silicone SE-555 were evaluated by measuring their continuous and intermittent stress-relaxation properties while the samples were in a vacuum at a temperature of 125°C.

By maintaining an elastomeric sample continuously at a fixed elongation (in this case 25%), the effects of chain scission in the sample are represented by a stress decay with time. When a sample of the material is maintained in the same environment in an unstretched state, and at periodic and widely-spaced intervals is rapidly elongated, its stress recorded, and is quickly returned to the unstressed condition, the force curve described by the recorded intermittent stress values reflects the net effect of scission and crosslinking. This technique, which gives a measure of chemical changes which occur in the polymer network, was developed by Tobolsky[1]; the measurements are collectively termed "continuous and intermittent stress-relaxation" tests.

The apparatus for the continuous and intermittent stress-relaxation measurements is described in the second part of this section.

Rings of the elastomers to be tested were cut from the 0.040-in (nominal) sheet stock furnished by the Jet Propulsion Laboratory. The measured thickness of eight rings varied from 0.039 to 0.053 inch (0.102 to 0.136 cm). The average inside and outside diameters of the rings were about 1.75 and 2.00 cm respectively. The diameters were calculated from the weights of a ring and a disc (from the inside of the ring), the thickness of the disc, and the density of the material. The equations used are:

$$D_i = \left[\frac{4\,W_D}{\pi T \rho}\right]^{1/2}$$

and

$$D_o = \left[\frac{4(W_D - W_R)}{\pi T \rho}\right]^{1/2}$$

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[1] A. V. Tobolsky, Properties and Structure of Polymers, John Wiley and Sons, Inc., 1960.

where D_i and D_o are the inside and outside diameters of a ring, W_D and W_R are the weights of the disc and the ring, and T and ρ are the thickness and density of the material.

The rings were then placed over the 1/8-inch diameter support rods of the sample holders (see Figure V-16) and the assembly mounted in the stress relaxometer. Ring specimens were used instead of dumbbell specimens because of the difficulty in determining the strain in the gage section of the latter, except by the use of bench marks on the specimen. With rings, the strain in the sample is directly related to the crosshead travel. Also, when the strain rate must remain constant and be precisely known, the testing of ring specimens is the only known method which can be readily employed to obtain data at a strain rate which remains constant throughout a test. (Dumbbell specimens were used out of necessity for testing the rather stiff plastic materials, since rings of these materials, cut from thin flat sheets, required appreciable forces to cause the rings to flatten out on the supporting rods. (Probably the easiest and best way to overcome this difficulty with stiff material would be to prepare the materials in the form of thin-walled tubes from which the rings could be sliced and which would have the proper shape for mounting on the supporting rods.) The theoretical and experimental aspects of employing rings instead of dumbbell specimens have been extensively discussed by Smith.[2] His data show the excellent agreement between the experimentally-determined strain rate from photographs of bench marks and the strain rate calculated from the crosshead speed and the average diameter of rings.

Twenty-eight hours after the vacuum system had been turned on (eleven hours after the heaters had been turned on) the constant and intermittent-stress relaxation measurements were begun. The relaxometers contained the following

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[2] T. L. Smith, Mechanisms of Reversible and Irreversible Loss of Mechanical Properties of Elastomeric Vulcanizates Which Occur at Elevated Temperatures, Technical Documentary Report No. ASD-TDR-62-572, Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, June 1962.

samples:

Relaxometer Station No.	Material
1, 8	Viton B
2, 7	Viton A
3, 6	Teflon TFE*
4, 5	Silicone-555 (red)

Prior to each measurement, the load cells were balanced and electrically calibrated to assure that there was no shift in the load cell output.

A staggered, logarithmic time schedule for the commencement and duration of tests on each relaxometer station and for subsequent load readings was used. Since the load cell outputs were recorded with a single-pen recorder, only one force at a time could be monitored. The samples which were to undergo continuous stress-relaxation tests in relaxometer stations 1, 2, and 4 (Viton B, Viton A, and silicone-555) were each strained to the predetermined 25% strain as indicated by the light indicator circuit readouts of the individual "bottom stops") in numerical order at successive six-minute intervals. The output from the load cell from each station was watched for six minutes after the sample's initial distention; then the next sample was distended and watched for six minutes, etc. Subsequent point readings of load were made on each station at expanding time intervals as dictated by uniformly-spaced points on a log-time chart. Once initially strained, these samples remained so for the entire duration of the tests.

Immediately following the last six-minute continuous stress-relaxation reading (relaxometer station 4), intermittent stress-relaxation tests were commenced at stations 5, 7, and 8 at successive five-minute intervals in numerical order. Each sample was rapidly extended to 25% strain and held there for about 2-1/2 to 3 minutes while the load cell output was observed; then the load was quickly removed from the sample. The intermittent force values used in plotting intermittent stress-relaxation curves were those measured after a sample had been at 25% strain for about 2-1/2 minutes. It was found that this period of

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* Dumbbell samples for constant strain rate tensile testing in vacuum after 850 hours.

time was required to eliminate the force decay effects due to viscous relaxation. A force-time trace recorded during one of the intermittent measurements on Viton B is shown in Figure V-1. The viscous-relaxation predominance during the first minute at 25% strain is apparent.

Because of the long time period (28 hours) required to obtain the equilibrium vacuum-thermal conditions prior to beginning the test, it was impractical to attempt to extrapolate the retractive forces f(t) to a zero-time retractive force f(0). The retractive force f(0) for the continuous measurements which we have used in the subsequent figures is a "best line" extrapolation to zero test time of the non-viscous portion of the six-minute force curve recording. For the intermittent case, the first data point is taken as f(0). Thus, in reality, the forces representing zero time in this work are actually the forces after 28 hours of vacuum, eight hours of which were at temperatures which gradually increased from room temperature to 125°C.

Under these particular conditions, previous tests dictated that in order to prevent anomalies arising from incomplete elastic recovery of the sample, a minimum interval of 0.5 hour in the relaxed state was allowed before subsequent intermittent measurements were made on the same specimen. After this initial interval, however, intermittent stretching to 25% strain was spread out in the usual logarithmically-expanding time scale.

Continuous and Intermittent Stress-Relaxation Results

Continuous and intermittent measurements were made at 25% strain and 125°C in vacuum for 850 hours. The results are shown in Figures V-2 and V-3.

The Viton B sample, stressed intermittently, broke after 27 hours. The sample had begun to show a slight increase in "modulus" at about 10 hours. The Viton B sample subjected to continuous strain exhibited a 50% degradation in strength in 37 hours. Almost the same rate of stress decay prevailed to the termination of the test at which time the Viton B sample retained about 25% of its original strength.

The intermittent Viton A sample broke after 4-1/2 hours; the stress had decayed 80% in the first hour. Because of the unexpected rapid failure of

this sample, a thorough check was made of the associated instrumentation and hardware. There were no equipment malfunctions, thus it was assumed that the sample was probably defective. (The intermittent curve for the Viton A measurements is not presented since it is felt it would be misleading.) The Viton A continuous curve shows a stress decay to zero shortly after 100 hours.

The silicone rubber (SE-555) continuous measurements show a 50% stress relaxation in eight hours. However, the rate of stress decay began to diminish at about the same time, and the change in stress was almost negligible after 300 hours at a stress level 28% of the original. The silicone rubber sample subjected to intermittent stress exhibited a stress increase to almost 500% of its original value in 360 hours. The sample was inadvertently broken during manipulation of the lower crosshead, so the response of the material to continued exposure to the vacuum-thermal environment is not known.

Photographs of new elastomer ring samples, and ring samples after 850 hours in a vacuum-thermal environment are shown in Figure V-4. Although both of the continuous and intermittent silicone samples are broken, they were broken through mishandling and not as a result of the in situ testing. All of the samples subjected to continuously stressed exhibit a permanent set with Viton A being the most pronounced. The continuously-stressed samples were still fairly flexible, and all could be bent 180° around a 1/16-in mandrel without fracture. Marked differences were observed in the samples subjected to intermittent stress. Both the Viton B and the silicone samples were flexible and could be bent double without breaking; on the other hand, the Viton A sample was rigid and brittle.

In Figure V-5, the relaxometer reflectors located above the samples are shown after the 850-hour vacuum-thermal run. (In addition to the three rubber samples, two Teflon TFE dumbbells were stored relaxed in positions 3 and 6 and extended at constant strain rate at the end of the run.) All of the reflectors were coated; however, the residues deposited on the Viton A reflectors were heavier than on the others.

From the limited amount of data obtained thus far, strong reservations should be exercised in making a qualitative or quantitative judgment about the relative stability of the various samples. Measurements similar to the ones

just discussed are planned on at least quadruplicate samples of the commercial elastomers Viton B, Viton A, Viton AHV and the silicone rubbers. From these data it is expected that comparisons as to their relative stability in a vacuum-thermal environment will be able to be made. Pursuant to the correlation of data obtained from the testing of the above commercial samples, it is anticipated that tests can be initiated on polymers synthesized at the Institute.

Constant Strain-Rate Tensile Measurements

Tensile stress-strain curves for Teflon TFE and Teflon FEP-100 were determined on unaged and vacuum-thermal-aged dumbbell specimens at 125°C. The purpose of this work was to determine if there are any detectable differences in the mechanical properties of these polymers which have been aged in a vacuum-thermal environment and then tested (1) in vacuum and (2) in air.

Dumbbell specimens (1/8-in gage width, 3/4-in gage length) were used instead of rings because of the stiffness of the polymers, as previously mentioned.

Two methods of determining strain in a sample may be used. Briefly, one method is to mark two (or preferably more) horizontal bench marks in the gage area and well away from the curved portion of a tensile specimen. By photographing the specimen at known time intervals as it is elongated, the distance between the bench marks may be recorded. The increase in distance between any two bench marks ($d-d_o$) divided by the original distance (d_o) is, of course, the strain at the known time. When it is not possible to view each sample while it is being tested, it becomes necessary to determine an effective gage length L_e of the dumbbell by relating the photographic bench mark data (preferably from two or more samples) to the crosshead speed (XHS) and the time (t) by the equation

$$\frac{d-d_o}{d_o} = \frac{XHS\ (t)}{L_e}$$

When L_e is determined for each material at the test conditions, it may be used with reasonable accuracy in subsequent measurements on the same material at the same test conditions (providing the properties of the material are not greatly

modified prior to the tensile test in which case L_e may change.) Since the samples in the relaxation units in the vacuum chamber were not visible it was necessary to determine an L_e for each material, and to record the crosshead speed during the test to be able to arrive at values of sample strain.

Constant Strain Rate Tensile Results

The results of constant strain rate tests performed on vacuum-thermal aged and unaged Teflon TFE dumbbell specimens are shown in Figures V-6, V-7, V-8 and V-9. Figure V-6 shows stress-strain curves at 125°C for duplicate specimens which were subjected to vacuum-thermal conditions for 850 hours, followed by conditioning in air at 125°C and straining to break on an Instron tester. The curves in Figure V-7 show similar data on unaged Teflon TFE specimens tested on the Instron. Comparison of the aged and the unaged specimens in Figures V-6 and V-7 shows that, within the experimental reproducibility of sample preparation and test measurements, the data are essentially coincident, and no mechanical properties change is apparent. In Figure V-8, tensile stress-strain data are shown for vacuum-thermal aged Teflon TFE, where one sample is tested in vacuum in the relaxometer and one is tested in air on the Instron. The curve for the sample tested in vacuum is uncertain; it is suspected that the temperature in this particular relaxometer was higher than the indicated 125°C. A repeat of this test is planned. Figure V-9 shows the stress-strain curve for a new Teflon TFE sample tested in air in a relaxometer unit, and the same stress-strain curve in vacuum as was shown in Figure V-8. The curve of the unaged Teflon TFE tested in the relaxometer is in good agreement with the curves on unaged Teflon TFE tested on the Instron (Figure V-7), indicating that the low stress values on the sample tested in vacuum were not due to instrumentation difficulties, but more probably to temperature inaccuracy as mentioned above.

Figure V-10 shows tensile stress-strain curves for unaged and vacuum-thermal aged Teflon FEP-100. A somewhat higher modulus was recorded for the sample that was aged in vacuum at 125°C for 850 hours. More samples would have to be tested before a valid qualitative comparison between the aged and the unaged materials could be made.

Creep Test Measurements

Constant-load creep curves for Teflon TFE, Teflon FEP-100 and two thicknesses of Mylar film were determined on air-aged and vacuum-aged samples at 125°C for up to 850 hours.

Shown in Figures V-11 and V-12 are creep results for Teflon TFE and Teflon FEP-100 respectively. Figure V-13 presents creep results for two Mylar films in air. No comparisons are made at present regarding the relative creep rates of these materials in air and in vacuum because of the need for a larger sample population.

APPARATUS AND PROCEDURES

Stress Relaxation Apparatus

Eight identical relaxometer assemblies are mounted in the vacuum chamber; another set of eight are mounted in an atmospheric oven.

The basic stress-relaxation test apparatus, as adapted for use in the vacuum chamber, is depicted in Figure V-14. A view of the eight stress-relaxometers at the conclusion of the 850-hour test is shown in Figure V-15. As indicated in Figure V-14, a sample of the elastomer in the form of a ring is mounted between two sample holders. The holders for supporting sample rings in the stress relaxometers are shown in Figure V-16. The upper holder is attached to a load cell and the lower sample holder is connected to a rack; the rack's pinion is driven from a gear box to position the lower sample holder with respect to the upper so as to distend the sample ring. When the sample ring is in a relaxed position, the lower sample holder is at its highest position; this position is determined by an adjustable stop and may be detected electrically when the sample holder makes contact with the stop. When the sample ring is in its strained position, the lower sample holder is in contact with a lower stop; this is also detected electrically. The position of the lower stop is adjusted at the beginning of the series of tests to correspond to a predetermined elongation. The gear-box drive for the rack and pinion is actuated by a crank rod which is mounted through a ball in the door of the oven and through an O-ring sealed spherical bearing in the vacuum chamber rear wall.

The relaxometers that are mounted in the vacuum chamber have heaters which are supplied with power from separate variable autotransformers and are made from two semicylindrical ceramic heating elements supported on a fired lava base as indicated in Figure V-14. A cylindrical copper sleeve prevents the sample from "seeing" the heating elements and thus promotes uniform heating of specimens. Bright chrome-polished reflectors are supported at the top of the furnace to isolate the sample from the cooled brass top plate; another single polished reflector rests at the base of the furnace. A thermocouple is mounted close to the sample ring. The top brass plate is water-cooled to trap volatile condensable materials and thereby to prevent sample contamination

which might result from diffusion of volatiles from chamber to chamber. The cooled plate also cools the load cells.

Load Cells

Each relaxometer station has its own load cell (8 in the vacuum chamber, 8 in the oven; 16 in all) consisting of a single Microdot 120-ohm temperature-compensated strain gage welded to a stainless steel cantilever beam which is mounted parallel to the top plate (See Figure V-17). The gage is centered between the free end of the stainless steel strip and the clamp. When a load is applied to the tip of the beam, a resistance change, linearly proportional to the applied load, occurs in the strain-sensitive element of the strain gage. The strain gage occupies the single active arm (R_4) of a wheatstone bridge. The change in the resistance of the strain gage due to the applied load is then exhibited as a voltage difference between two points on the wheatstone bridge, again linearly proportional to the applied load. After appropriate calibration with dead weights, this difference is interpreted directly as a linear indication of the applied load. This voltage difference is measured and recorded using an L & N single-pen, potentiometric "Speedomax H" recorder.

The strain gage itself is temperature compensated; it is designed with a resistance/temperature slope so that when it is mounted on the stainless steel beam, the error due to differential thermal expansion of the beam and gage is minimized.

Four electrical calibration points (25, 50, 75, and 100% of full load), consisting of resistors switched into parallel with R_1 or R_3, are provided to check the output slope from the strain gage.

Changes in the readout instrumentation which could conceivably cause a "zero shift" -- a source of error -- are detectable by reversing the polarity of the output from the bridge into the readout. The difference between simultaneous readings with normal and reversed polarity indicate the exact mode and magnitude of the "drift."

The relaxometers for use in an inert gas environment utilize Statham 350-ohm load cells with integral 4 active-arm bridges; these are also supplied with power from Zener-controlled sources.

Creep Apparatus

Creep tests at constant load are performed on the JPL-supplied, commercial plastic materials: Teflon TFE, Teflon FEP-100, Mylar films, and nylon. (Preliminary creep results are presented earlier in this section.) The creep apparatus constructed for this program was described in the Interim Technical Report No. 1, June 8, 1963.

Vacuum System

The vacuum chamber and associated control and recording equipment were discussed in detail in the Interim Report. A picture of the chamber with complete instrumentation is shown in Figure V-18.

Procedures Preparatory to Initiating Stress Relaxation Measurements in Vacuum

As previously mentioned, stress relaxation measurements were not begun in vacuum until about 28 hours after the evacuation of the chamber was started. Some of the reasons for this time delay are:

1. Many hours were required to attain a suitable "cold" vacuum because of sample out-gassing;
2. Heat was applied slowly to the system to prevent destruction of the samples by local overheating;
3. Considerable out-gassing was experienced when elastomer samples were heated, requiring additional pump-down time;
4. Once the general temperature region of 125°C was reached, additional time was required for final adjustment of the power to each relaxometer to maintain the sample at 125°C.

The procedures employed in preparing for the first 850-hour vacuum-thermal test (from setting the 25% strain position in each relaxometer to reaching "steady-state" operating conditions) were as follows: Ring specimens were laid on a flat surface and pinched together by hand, without straining the specimens, into the shape of a rubber band. While in this shape (which is the shape they assumed when actually strained), two bench marks were placed on

them about one-half inch apart. The precise distance between the marks was then measured using an upright cathetometer.

The rings were then mounted unstrained in their respective test stations and were subsequently individually strained 25% using the upright cathetometer to determine directly the separation of the bench marks. The lower stop of each relaxometer was adjusted and locked at the 25% strain position. Continuity lights were used to indicate that contact had been made and, therefore, the lower strained positions reached. The rings were then relaxed and removed, and new, unmarked, unstrained rings were inserted. (Two Teflon TFE 20-mil plastic dumbbells for constant strain rate tests were also inserted in relaxometer positions 3 and 6. The lower stops in this case were set at the bottom of the relaxometer chamber to allow maximum strain.)

The vacuum system was closed and isolated and evacuation begun. The load cells were also turned on at this time. About twenty hours later, with the system at 2.0×10^{-5} mm of Hg, the relaxometer heaters were turned on.

Heat was first applied to the Teflon TFE dumbbells in relaxometer stations 3 and 6 producing a heating rate average of 1°C/min. As the temperature increased to 125°C, there was a pronounced change in the chamber pressure to 2.5×10^{-4} mm of Hg and a subsequent slight recovery to 1.2×10^{-4} mm of Hg. Operating temperature of 125°C was achieved 2.25 hours after heat was applied.

With the system at 1.2×10^{-4} mm of Hg, heat was then applied to the Viton B rubber rings in relaxometer positions 1 and 8, at an average heating rate of about 25°C/min, accompanied by a rapid loss of chamber pressure to 1×10^{-3} mm of Hg, followed by a slow recovery to 1.2×10^{-4} mm of Hg. Operating temperature was achieved approximately five minutes after heat was initially applied.

Heat was then applied in turn to the Viton A samples and the silicone-555 (red) samples. In each case, the chamber pressure increased somewhat as the samples were heated. After about 25 hours of elapsed time since evacuation was first begun, the pressure was 2.5×10^{-4} mm of Hg. About three more hours were required to make final adjustments to the eight individual relaxometer heaters to establish temperature equilibrium at 125°C in each

unit. Some 28 hours after evacuation was begun, the stress-relaxation measurements were initiated.

It is desirable that the time to achieve test conditions be reduced to a minimum, and it appears that by modifying the procedures the time can be shortened considerably.

The test equipment for performing stress relaxation and creep tests in air at 125°C were described in the Interim Report No. 1. Essentially, duplicates of the equipment mounted in the vacuum chamber are mounted in an electric oven (Freas Model 124-13, 25 x 19 x 19 inches chamber size), except that individual specimen heaters are not required since the oven is controlled at 125°C. The relaxometers are remotely operated by means of a rod through a ball joint in the oven door.

The twin relaxometer for performing stress relaxation tests on samples in an inert gas environment at 1 atm pressure and 125°C was described in the Interim Report No. 1.

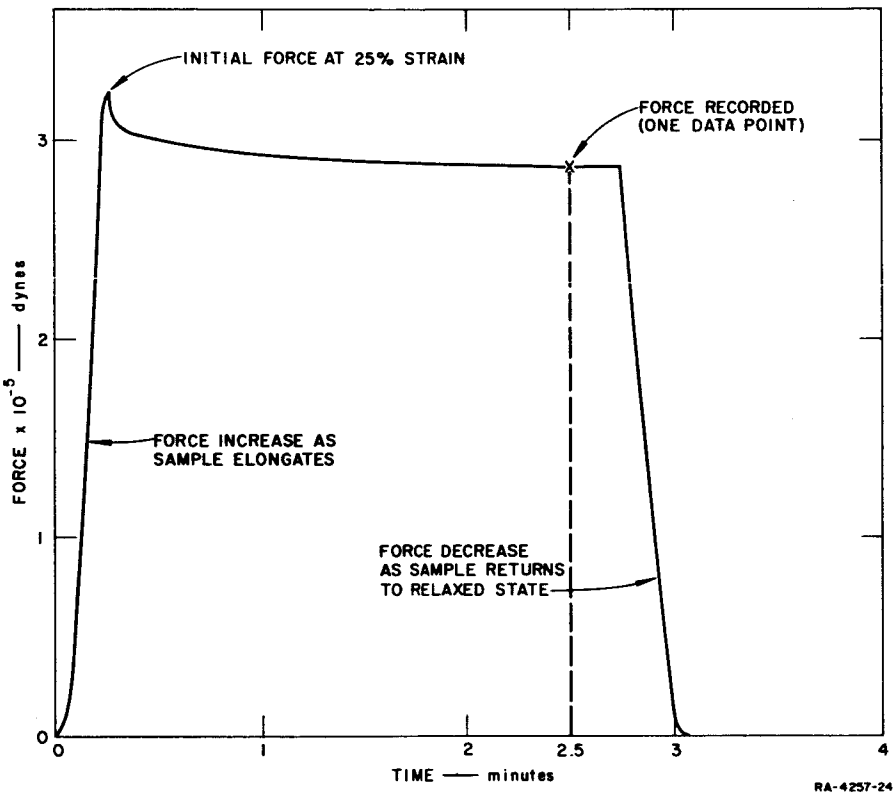

FIG. V-1 FORCE-TIME TRACE RECORDED DURING A SINGLE INTERMITTENT STRESS MEASUREMENT AT 125°C ON VITON B (Du Pont)

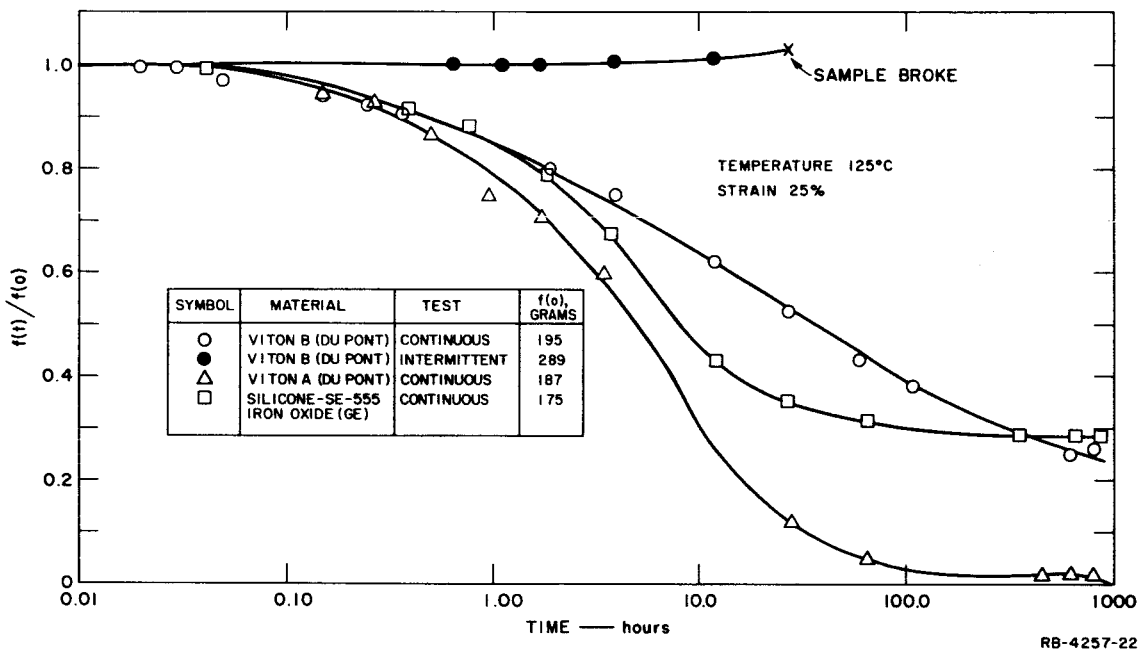

FIG. V-2 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR VITONS AND SILICONE ELASTOMERS

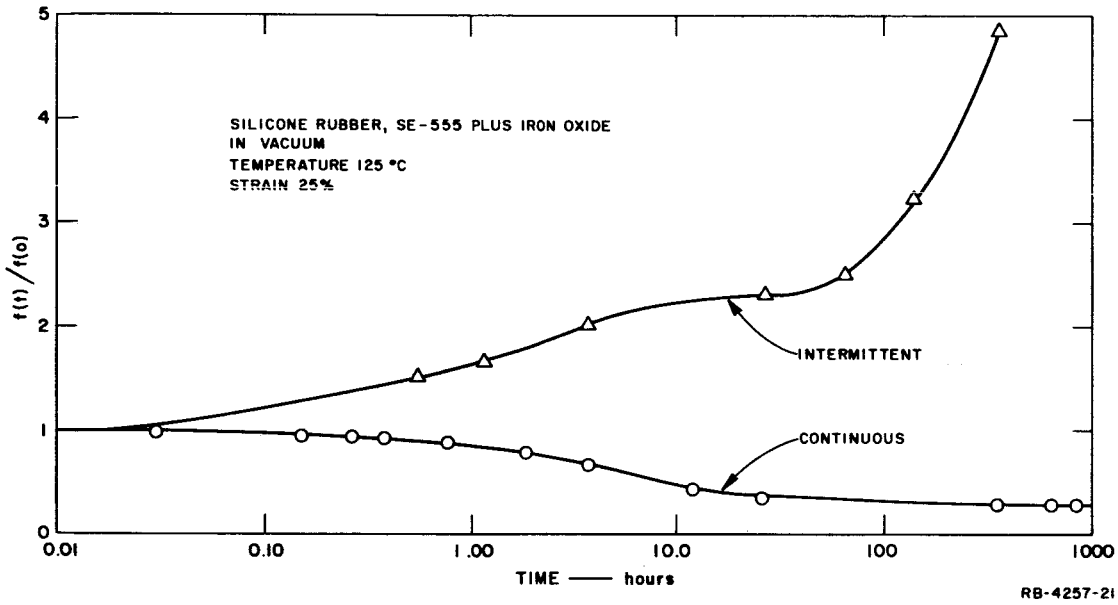

FIG. V-3 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR A SILICONE RUBBER

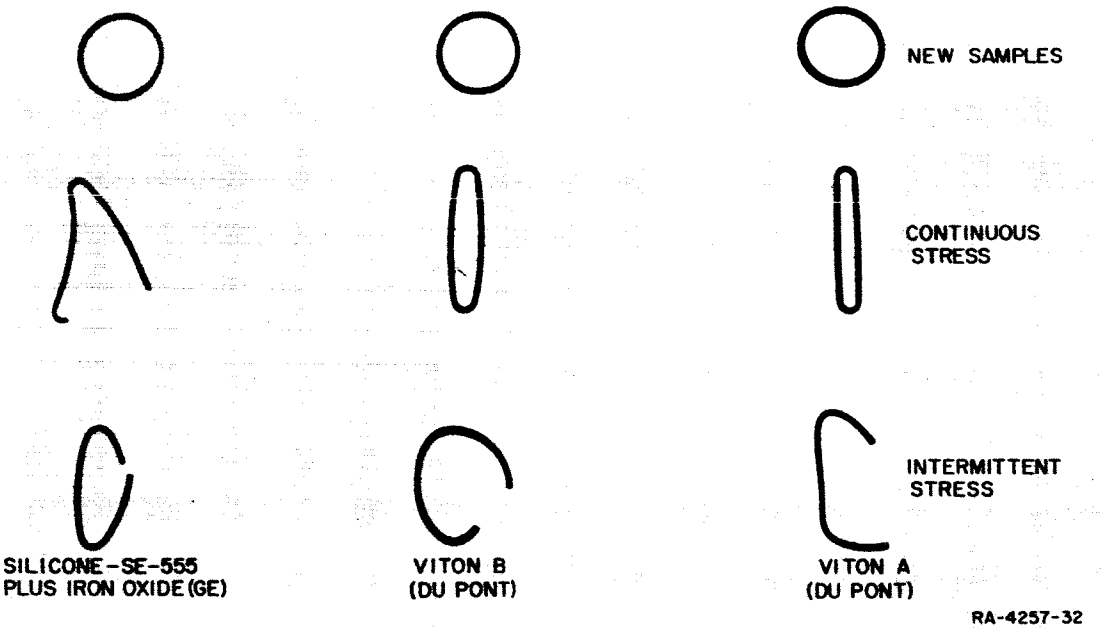

FIG. V-4 ELASTOMER RING SAMPLES AFTER 850 HOURS IN VACUUM-THERMAL ENVIRONMENT

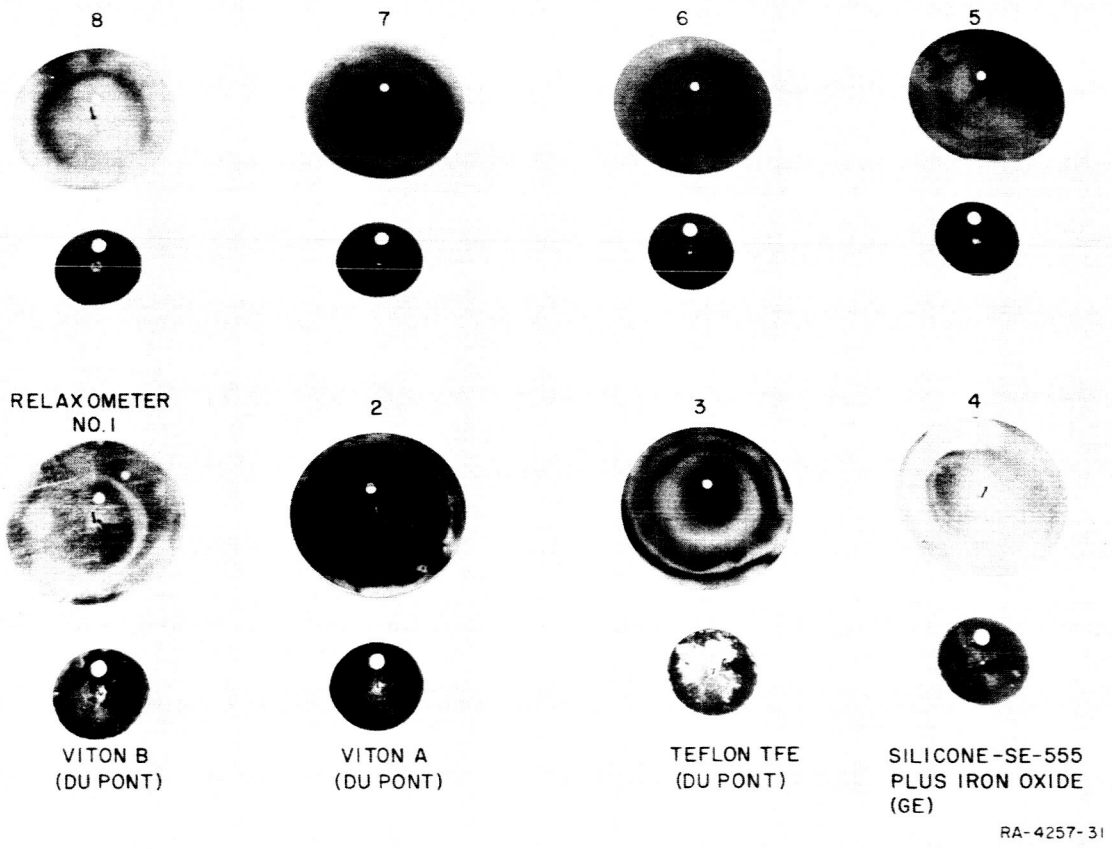

FIG. V-5 APPEARANCE OF RELAXOMETER REFLECTORS AFTER 850-HOUR VACUUM-THERMAL RUN

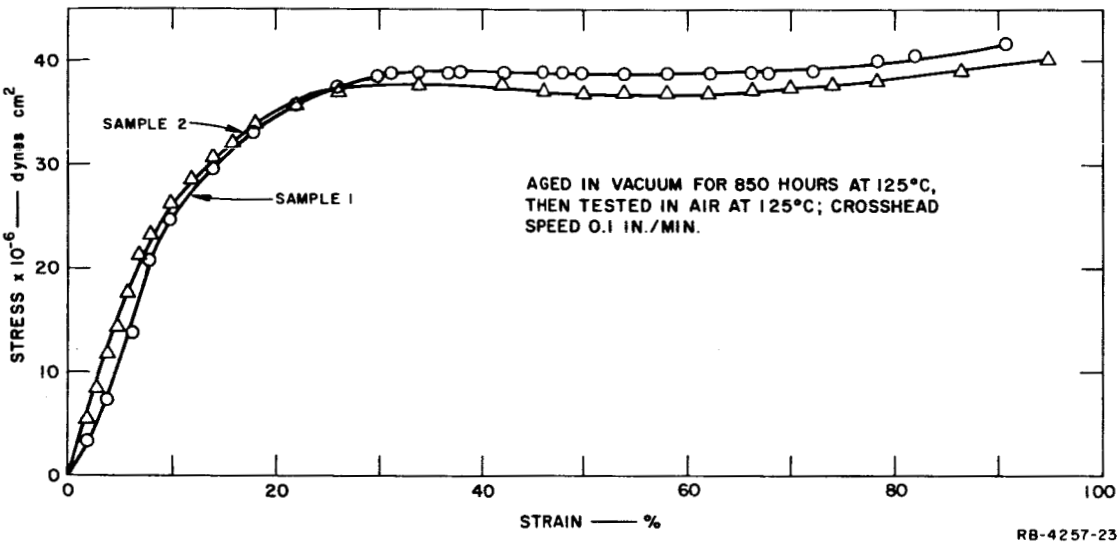

FIG. V-6 TENSILE, STRESS-STRAIN RESULTS FOR VACUUM-AGED TEFLON TFE

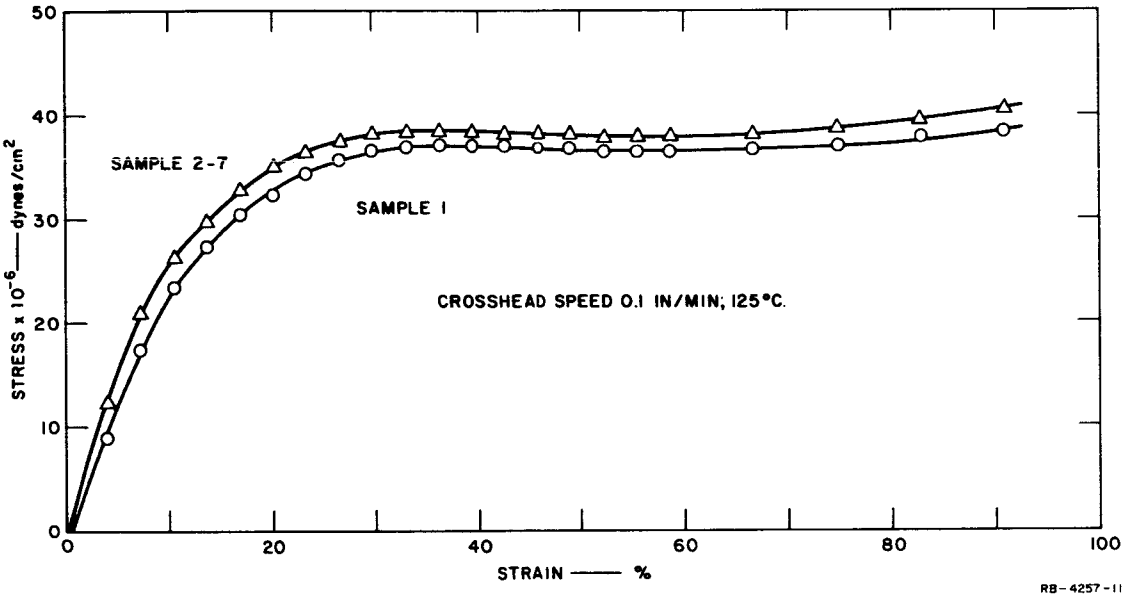

FIG. V-7 TENSILE, STRESS-STRAIN RESULTS FOR UNAGED TEFLON TFE

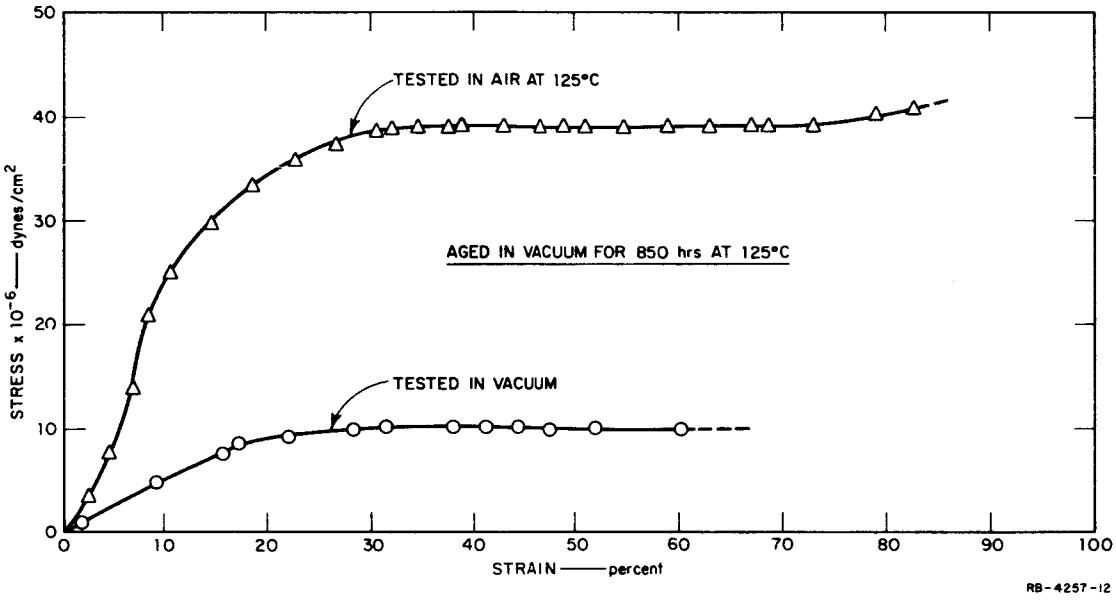

FIG. V-8 TENSILE, STRESS-STRAIN RESULTS FOR VACUUM-AGED TEFLON TFE, TESTED IN VACUUM AND IN AIR

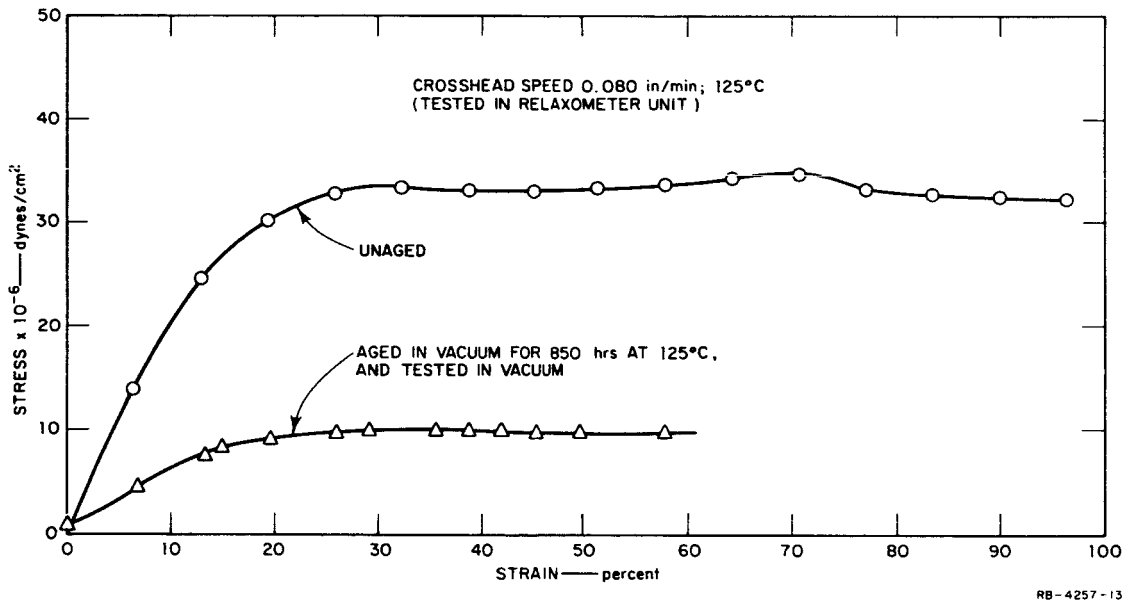

FIG. V-9 TENSILE, STRESS-STRAIN RESULTS FOR UNAGED AND VACUUM-AGED TEFLON TFE

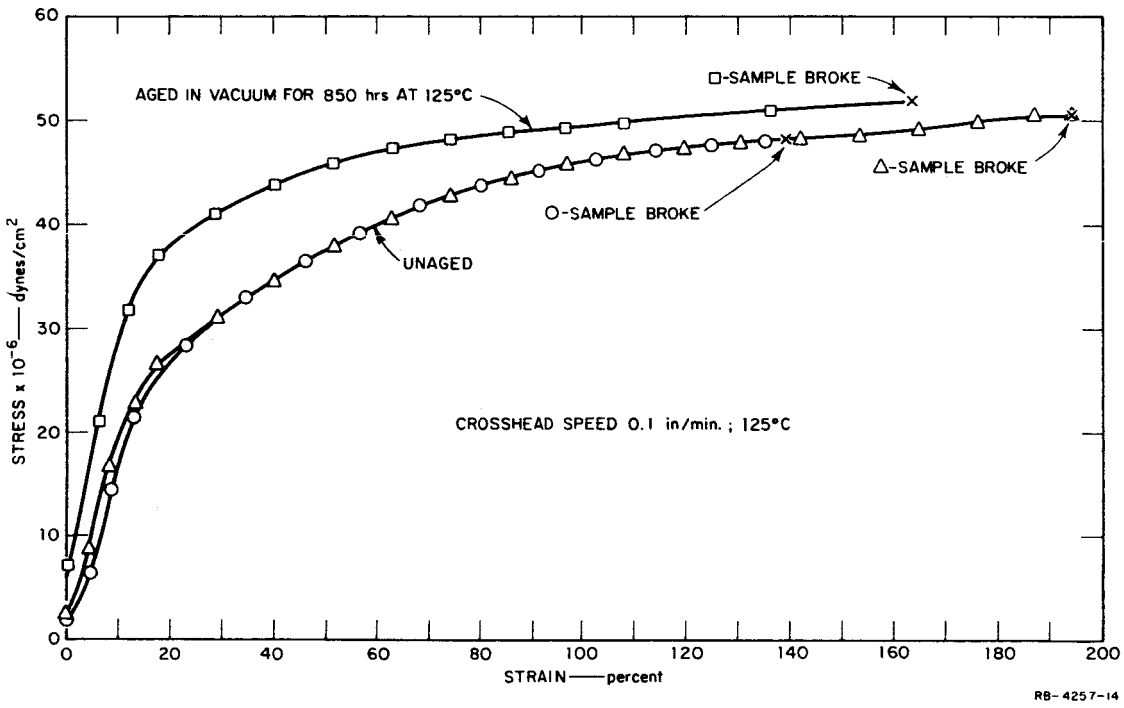

FIG. V-10 TENSILE, STRESS-STRAIN RESULTS FOR UNAGED AND VACUUM-AGED TEFLON FEP-100

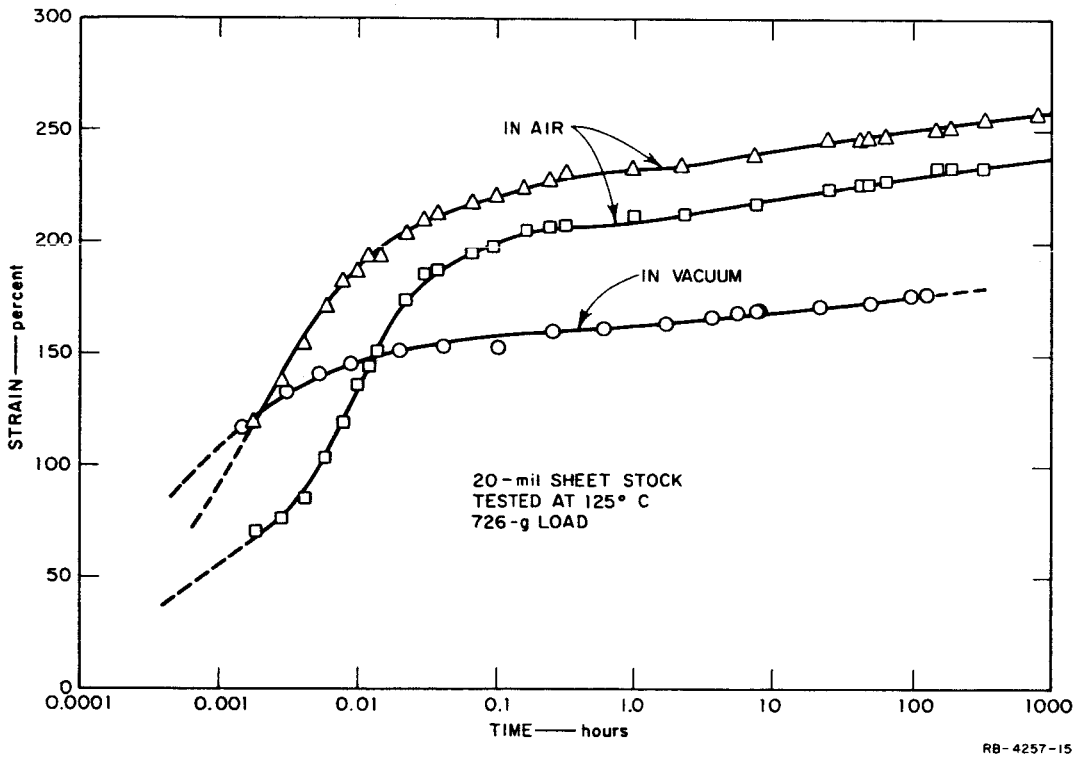

FIG. V-11 CREEP TEST RESULTS FOR TEFLON TFE IN AIR AND IN VACUUM

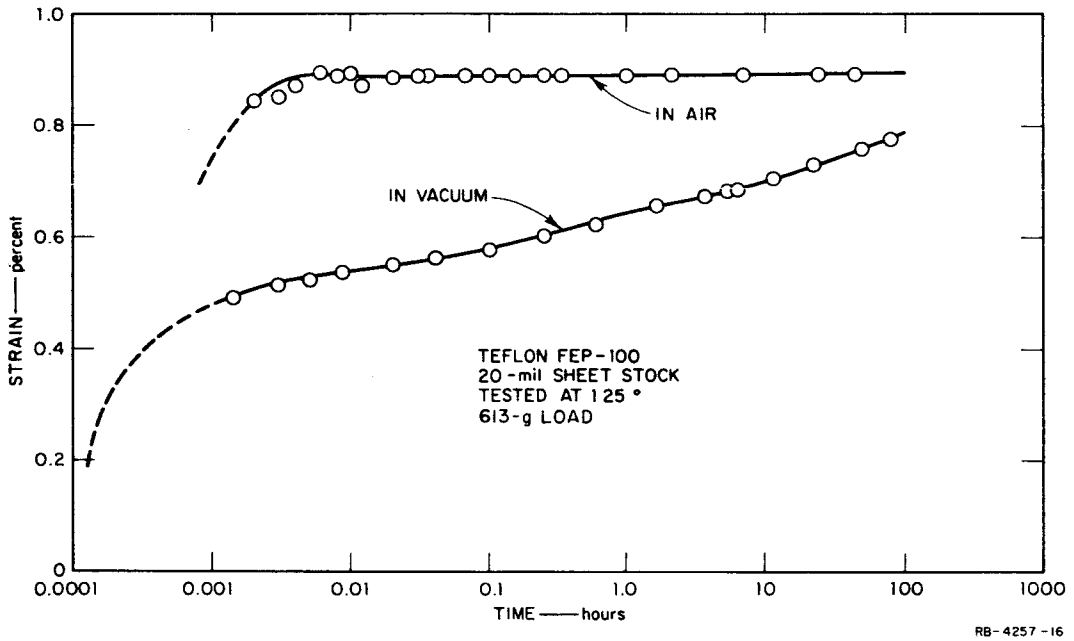

FIG. V-12 CREEP TEST RESULTS FOR TEFLON FEP-100 IN AIR AND IN VACUUM

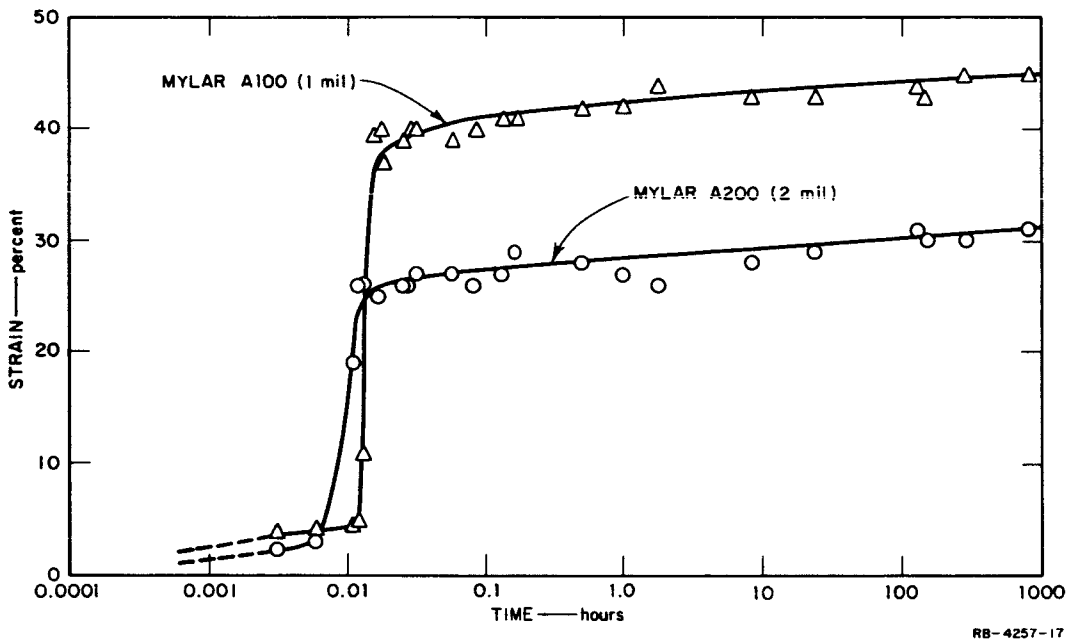

FIG. V-13 CREEP TEST RESULTS FOR MYLAR FILMS IN AIR ENVIRONMENT AT 125°C

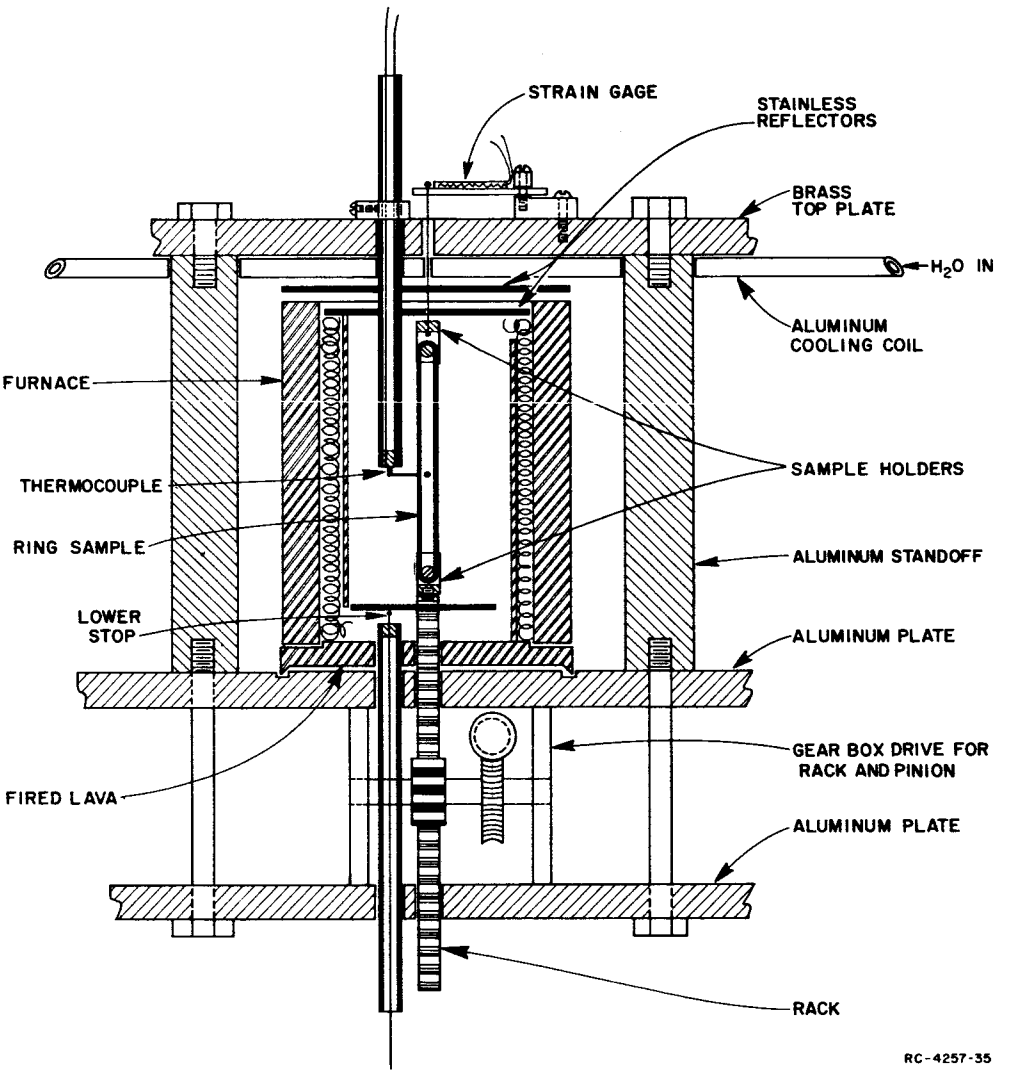

FIG. V-14 SCHEMATIC ASSEMBLY DRAWING OF RELAXOMETER

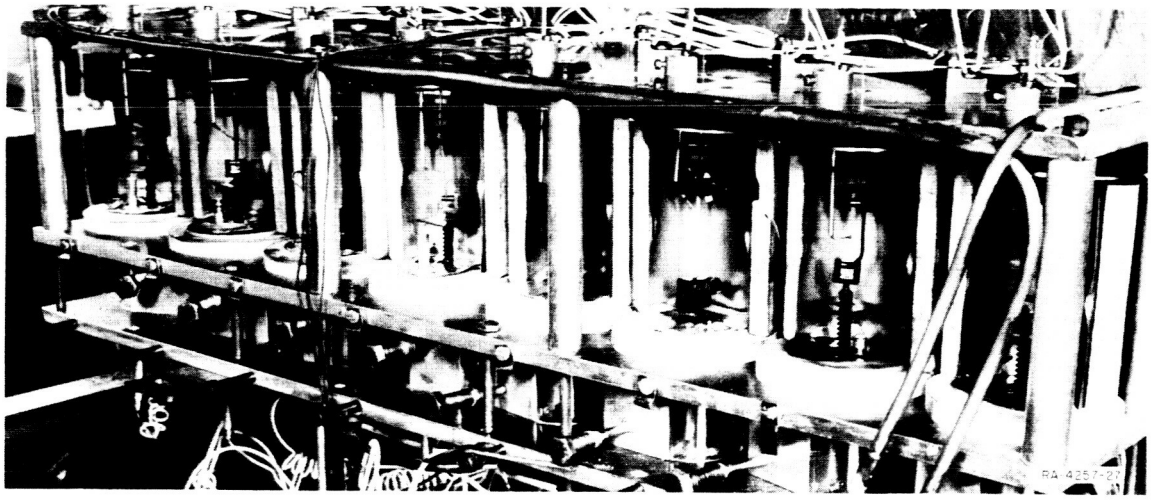

FIG. V-15 VIEW OF VACUUM STRESS RELAXOMETERS (With Samples in Place) AFTER 850-HOUR TEST

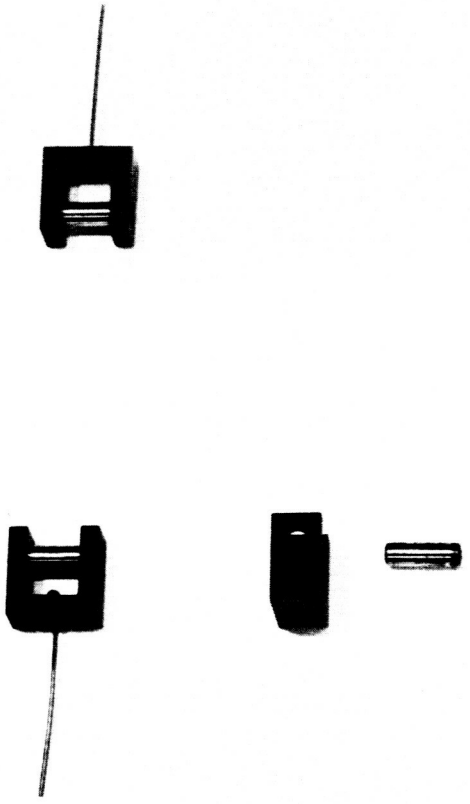

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FIG. V-16 HOLDERS FOR SUPPORTING ELASTOMER RING IN STRESS RELAXOMETER

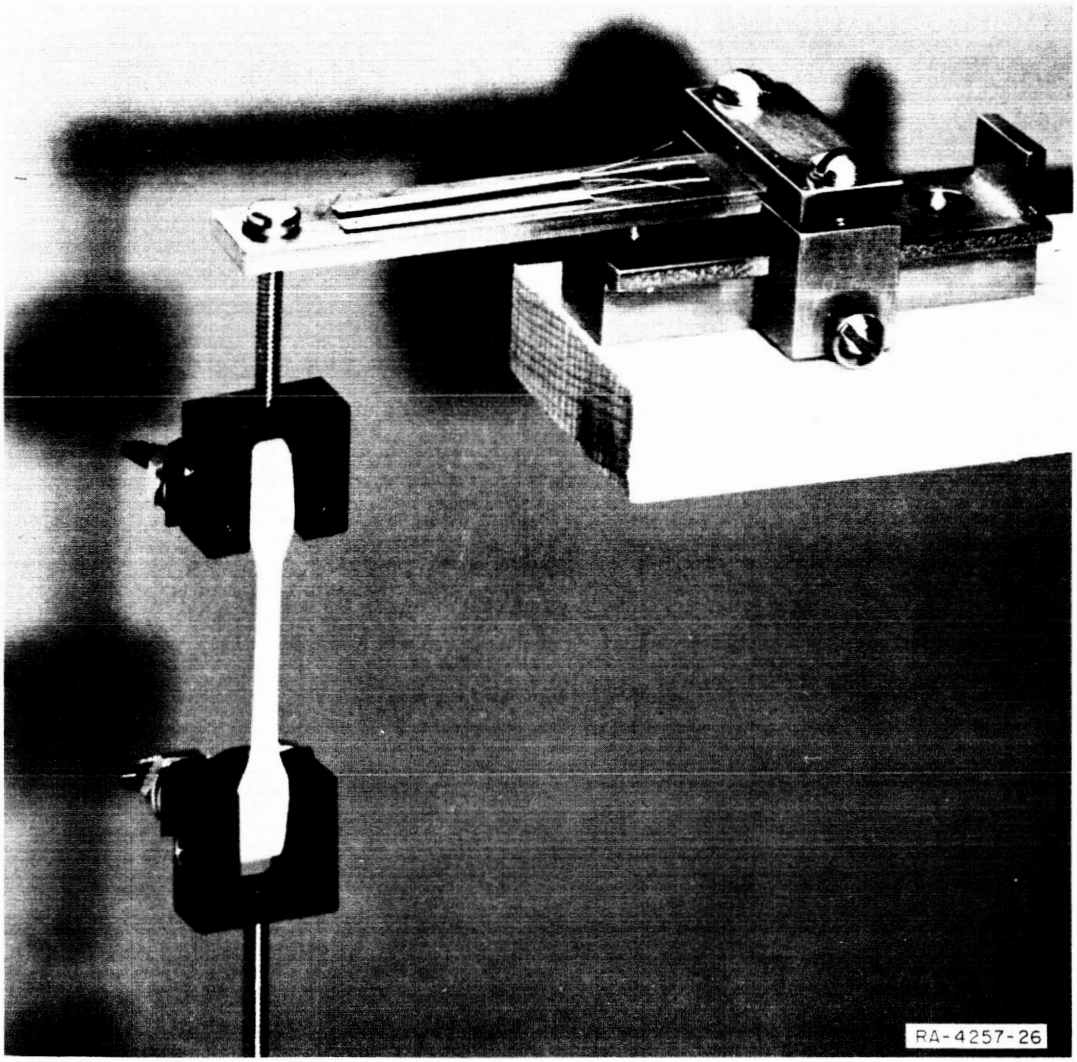

FIG. V-17 MOCK-UP OF CANTILEVER BEAM LOAD CELL FOR OPERATION IN VACUUM AND AT ELEVATED TEMPERATURES

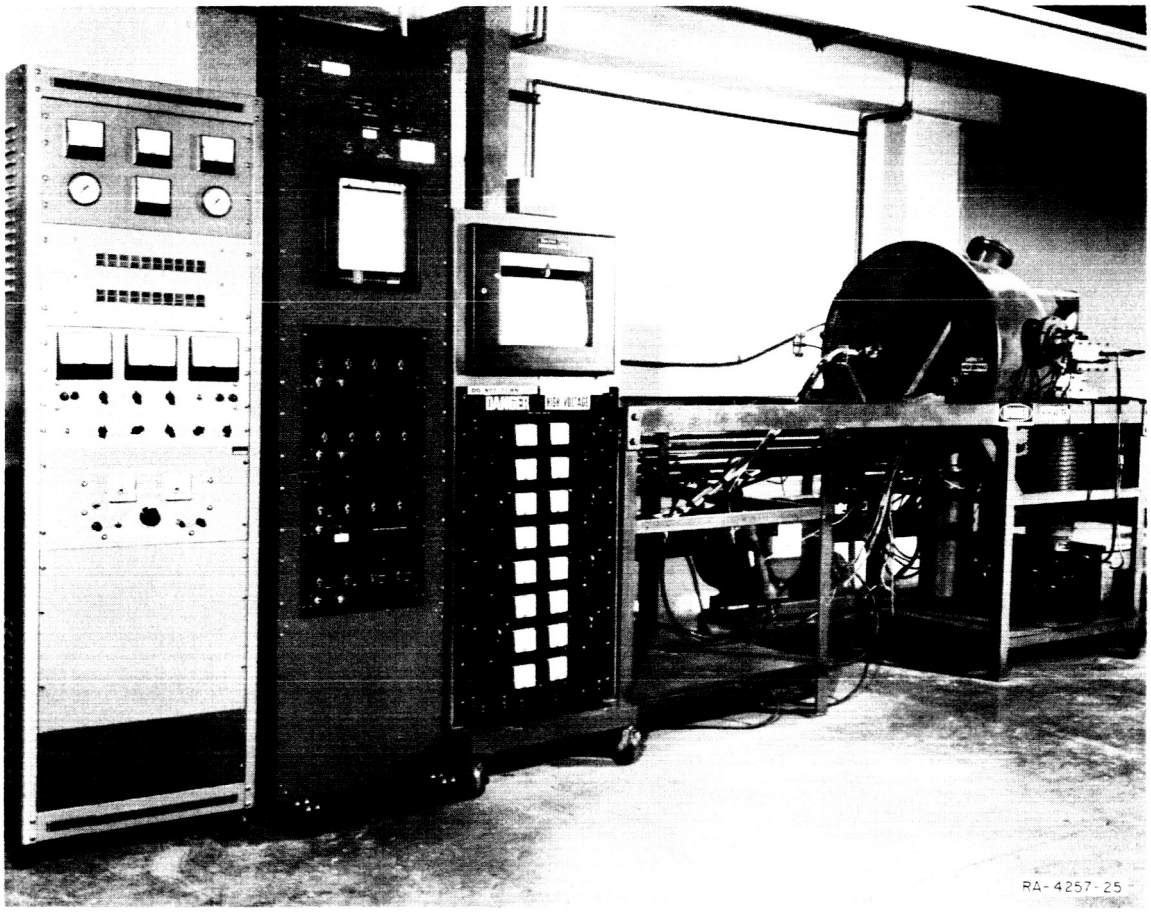

FIG. V-18 VACUUM CHAMBER AND ASSOCIATED INSTRUMENTATION